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INTERNATIONAL ATOMIC ENERGY AGENCY
AGENCE INTERNATIONALE DE L'ÉNERGIE ATOMIQUE
МЕЖДУНАРОДНОЕ АГЕНТСТВО ПО АТОМНОЙ ЭНЕРГИИ
ORGANISMO INTERNACIONAL DE ENERGÍA ATÓMICA

REPORT

ON

THE PROFICIENCY TEST EXERCISE

FOR

X-RAY FLUORESCENCE LABORATORIES

ORGANIZED BY

INTERNATIONAL ATOMIC ENERGY AGENCY

PTXRFIAEA/01/MAY-2002

IAEA Laboratories, Seibersdorf
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FOREWORD

The main role of the International Atomic Energy Agency as described in its statute is to assist research on, and development and practical application of, atomic energy for peaceful uses throughout the world and to perform any operation or service useful in research on, or development or practical application of, atomic energy for peaceful purposes. Nowadays, one of the important activities involving international cooperation and exchange of scientific and technical information is introduction of the quality assurance and quality control protocols (QA/QC) in the analytical laboratories. In recent years this process has been intensified, especially in laboratories that have to provide their services on market. Introduction of QA/AC protocols into the analytical work, if performed in an orderly way, leads to more reliable services and improved analytical results. However, it requires additional material resources and increases the workload for the laboratory staff. The Agency's Laboratories in Seibersdorf have long experience with QA/QC systems, especially in the radioactivity dose measurements and nuclear instrumental methods. There are many analytical techniques utilized here, including also X-ray fluorescence (XRF) spectrometry. This technique, due to its multielemental capabilities, good detection limits and well established quantitative analysis procedures for different kind of samples is applied widely for chemical composition analysis. It is also important that the cost of XRF analysis per sample/element is relatively low, as compared to other instrumental analytical methods. The XRF techniques have been introduced to many laboratories in the developing countries within the framework of technical cooperation projects guided by the Agency. In order to utilize the XRF equipment efficiently the Agency's Laboratories and the X-ray Group of the Instrumentation Unit are providing fellowship-training services in the application of XRF technique and evaluating the XRF equipment. Moreover, the Agency's Laboratories coordinated international research and application programs offer technical guidance and expertise in response to specific requests of the Member States. Due to a noticeable and growing interest in implementation of QA/QC systems in the Member States' XRF laboratories, as measured by an increasing number of training requests, as well as the competitive stress from the other analytical techniques, the services in QA/AC procedures have become the important activities of the Agency's Laboratories XRF Group. The proficiency test scheme for XRF laboratories has been initiated in order to provide a cost-free service for the Agency's Member States allowing the laboratories to control and improve their analytical performance. The participation in the proficiency testing exercises, at least once a year, is a must for the laboratories willing to follow QA/QC protocols. One has to emphasize that also the laboratories that have not yet implemented the QA/QC procedures can profit from participating in the proficiency test exercise. Participating in the test gives them a reference point and a basis for comparing their performance versus the performance of similar laboratories. It also gives them indications what could be improved in the their analytical practice. On a long term the participating laboratories can create a record of their performance and eventually can see a return on the investments in the QA/QC systems, the achieved improvements and/or sustained good analytical performance. When the results of the proficiency test exercise do not adhere to laboratory expectations this fact cannot be used to punish the analyst and in no way penalize the laboratory staff. The results should only be used as guidance on what could be improved in the analytical process and give the laboratory a better understanding what is their fit-for-purpose status.

INTRODUCTION

In 1997/98 the Agency's Laboratories XRF Group, Instrumentation Unit organized an intercomparison survey in order to gather information on the XRF laboratories, assess their analytical performance and identify major problems in the analytical work. The present proficiency test exercise, codenamed PTXRFIAEA/01, is expected to be a first in a sequence of rounds to be conducted on a yearly basis. Each round involves distributing a homogenous material to a number of laboratories where the material is analyzed with XRF techniques operated under routine analytical conditions. The distributed material is well characterized, but the assigned concentrations of the analytes, known to the organizers, are not given to the participants. The participating laboratories have usually three months to perform the analysis and to report the results including their uncertainties. Next the results are processed, grouped versus analytes/laborartories and a comparison of the assigned values of analytes with the values provided by participants is carried out by calculating *z*-scores and *u*-scores. From each round a report is made and distributed to the participating laboratories to provide them with the information on their performance and to let them decide if their analytical results are satisfactory based on their fit-for-purpose criteria. All the results submitted by the laboratories are anonymous. Each laboratory is assigned a code number, the link between the laboratory code and the laboratory name is known only to the organizers and to the laboratory itself.

DEFINITIONS AND TERMINOLOGY

To make a common base for understanding for all participants we provide several definitions of terms used in proficiency testing schemes. Although, this terminology might be known to some of the participants and can be found elsewhere [1, 2, 3] we want to make sure that terms used in this report are clearly defined and used without ambiguity:

Proficiency Testing Scheme: methods of checking laboratory performance by means of interlaboratory tests, sometimes called "round robin study".

True Value: the actual concentration of the analyte in the matrix.

Assigned Value: the value of the concentration of the analyte in the matrix used as the true value by the proficiency testing coordinator in the statistical treatment of results (or the best available estimate).

Target Value for Standard Deviation: a numerical value for the standard deviation of a measurement result, which has been designated as a target for measurement quality.

Consensus value: the mean value of the reported laboratory results after removal of the outliers.

Consensus value of the standard deviation: the standard deviation of the mean value of the reported laboratory results after removal of the outliers.

Certified Reference Material: A reference material, accompanied by a certificate, one or more of whose property values are certified by a procedure which establishes traceability to an accurate realization of the unit in which the property values are expressed, and for which each certified value is accompanied by an uncertainty at a stated level of confidence.

DETAILS

Test Sample

The test sample was the IAEA reference material IAEA-SL-1, Sediment Lake. Originally, the sediment sample was collected and prepared by US Department of Agriculture, Agricultural Research Service, USDA Sedimentation Laboratory, Oxford, Mississippi, USA and then it was donated to the Agency. The sediment was collected at the Sardis Reservoir, Panola County, Mississippi, USA. It was taken at the water depth of 15 m. The details of the homogeneity testing and full results as well as the details of the certification procedure can be found elsewhere [4]. The test samples have been repacked and distributed to participants together with the instructions for the analysts.

Assigned Value and Target Standard Deviation

The consensus values established during the intercomparison survey on IAEA-SL-1 reference material, published in report [4], were used as the assigned values of the analytes, X_A. 34 analytes were considered in this proficiency test round: Na_2O, MgO, S, K_2O, CaO, TiO_2, MnO, Fe_2O_3, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Mo, Sb, Cs, Ba, La, Ce, Nd, Hg, Pb, Th, and U. For each analyte a target value of the standard deviation has been assigned using a modified Horowitz function as proposed in the reference [5]:

$$H_A = \begin{cases} 0.22X_A & X_A < 1.2\cdot10^{-7} \\ 0.02(X_A)^{0.8495} & 1.2\cdot10^{-7} \le X_A \le 0.138 \\ 0.01\sqrt{X_A} & X_A > 0.138 \end{cases} \qquad (1)$$

In Eqn. (1) the assigned value of analyte, X_A, is expressed in terms of mass fraction. The target value of the standard deviation, σ_A is related to H_A by a factor k:

$$\sigma_A = kH_A, \quad k = 0.5, 1.0, 1.5 \qquad (2)$$

Depending on the value of the factor k the target value of the standard deviation is recognized as fit-for-purpose at three levels of uncertainty: k = 0.5, appropriate for high precision analysis; k = 1.0, appropriate for well established routine analysis; k = 1.5, satisfactory for common analytical tasks. The relative value of the target standard deviation, *RSD*, expressed in per cent, is defined as follows:

$$RSD = \frac{\sigma_A}{X_A}\cdot 100\% \qquad (3)$$

The relative value of the target standard deviation as a function of the assigned mass fraction of the analyte, X_A, is presented in Fig. 1.

Z-Scores and *U*-Scores.

The reported concentrations of analytes were compared with the assigned values using the *z*-score analysis. For every result a *z*-score was calculated:

$$z = \frac{x - X_A}{\sigma_A} \tag{4}$$

The term '*x*' denotes the reported mass fraction of analyte. Depending on the fit-for-purpose range of the target standard deviation, as defined in Eqn. (2), three different values of *z*-scores were calculated by combining Eqns. (2) and (4). Assuming that appropriate values for X_A and σ_A have been used and that the underlying distribution of analytical errors is normal, apart from outliers, in a well-behaved analytical system *z*-scores would be expected to fall outside the range $-2 \le z \le 2$ in about 4.6% of instances, and outside the range $-3 < z < 3$ only in about 0.3%. Therefore, based on the z-scores the following decision limits were established:

$$\begin{aligned} |z| &\le 2 && \text{- a satisfactory result,} \\ 2 < |z| &< 3 && \text{- the result is considered questionable,} \\ |z| &\ge 3 && \text{- the result is considered unsatisfactory.} \end{aligned} \tag{5}$$

The advice to the laboratory is that falling for the fit-for-purpose range selected by the laboratory, any *z*-score for an element outside the range $-2 \le z \le 2$ should be examined the analyst and all steps of the analytical procedure verified to identify the source(s) of the analytical bias.

For every participant the rescaled sum of *z*-scores, *RSZ*, as well as the sum of squared *z*-scores, *SSZ*, were calculated as defined by the following equations:

$$RSZ = \frac{\sum_{i=1}^{L} z_i}{\sqrt{L}} \tag{6}$$

$$SSZ = \sum_{i=1}^{L} (z_i)^2 \tag{7}$$

The symbol '*L*' denotes the number of results provided by the laboratory/participant for all the analytes determined. The summing up in Eqns. (6) and (7) takes into account all *z*-scores for all analytes reported by participant. The *RSZ* can be interpreted as a standardized normally distributed variable, with expected value equal to zero and unit variance. It is sensitive in detecting a small consistent bias in an analytical system, however, it is not sensitive in cases where there are even big errors but having opposite signs. The *SSZ* takes no account of the signs because it depends on the squared *z*-scores. It has a chi-squared (χ^2) distribution with *L* degrees of freedom. The *SSZ* can be regarded as complementary to *RSZ*, which means that if *RSZ* is well within the range $-3 < RSZ < 3$ and if at the same time value of *SSZ* is above the $\chi^2_{critical}$ value the overall performance of the laboratory requires improvement.

The reported results were accompanied by the standard uncertainty estimate made by the participant. The values were used to calculate *u*-scores:

$$u = \frac{|x - X_A|}{\sqrt{(\sigma_A)^2 + (\sigma_x)^2}} \tag{8}$$

The symbol 'σ_x' denotes the standard uncertainty of the reported result x. If the assumptions about X_A and σ_A and about the normality of the underlying distributions are correct, and the laboratory estimate of σ_x takes into account all the significant sources of uncertainty, the u-scores would have a truncated normal distribution with unit variance. In a well-behaved analytical system only 0.1% of u-scores would fall outside the range $u < 3.29$. Therefore, the following decision limits for the u-scores were established:

$1.64 \geq u$ - reported result does not differ from the assigned value,
$1.64 < u \leq 1.95$ - reported result probably does not differ from the assigned value,
$1.95 < u \leq 2.58$ - it is not clear whether the reported and assigned values differ, (9)
$2.58 < u \leq 3.29$ - reported result is probably different from the assigned value,
$3.29 < u$ - reported result differs from the assigned value.

The u-scores are especially useful for deciding whether the laboratory fit-for-purpose criteria are fulfilled. By comparing Eqn. (4) and Eqn. (8) one can immediately notice that for corresponding values of u-score and z-score the following inequality is always fulfilled:

$$u < z \tag{10}$$

It implies that if the u-score falls outside the range $u < 3.29$ also the decision limit for the corresponding z-score is triggered and the laboratory has to check the analytical procedure as well as review the uncertainty budget estimation. If u-score stays within the range $u < 1.64$ but at the same time the z-score decision limit is triggered ($|z| > 3$) the laboratory should reevaluate its fit-for-purpose status for the particular analyte.

Consensus Values

In order to get a general impression on the performance of the XRF technique applied by all the participants the reported results have also been treated in a way as they would be the results of the an intercomparison survey. The results were sorted and then tested for the presence of outliers using a set of seven outlier rejection tests:

description of symbols:

$x_1 < ... < x_n$ - set of analytical results,
$\bar{x}$ - mean value, (11)
s - standard deviation,

1. Coefficient of kurtosis [6], number of results: $5 \leq n \leq 100$, two-sided test, confidence level = 0.95:

$$b_2 = \frac{n\sum_{i=1}^{n}(\bar{x}-x_i)^4}{\left[\sum_{i=1}^{n}(\bar{x}-x_i)^2\right]^2} \tag{12}$$

- if b_2 > critical value then reject the result that is at the furthest distance from the mean, decrease n, repeat the procedure until $b_2 \leq$ critical value.

2. Coefficient of skewness [6], number of results, $5 \le n \le 60$, one-sided test, confidence level = 0.95:

$$\sqrt{b_1} = \frac{\sqrt{n}\sum_{i=1}^{n}(x_i - \bar{x})^3}{\left[\sum_{i=1}^{n}(x_i - \bar{x})^2\right]^{3/2}} \tag{13}$$

- if $\left|\sqrt{b_1}\right|$ > critical value then: if $\sqrt{b_1}$ is positive then reject x_n, otherwise reject x_1, decrease *n*, repeat the procedure until $\left|\sqrt{b_1}\right| \le$ critical value.

3. Veglia's test [7, 8], number of results: $4 \le n \le \infty$, two-sided test, confidence level = 0.95:

$$h = \sqrt{\frac{n}{n-1}}\frac{\left|x_k - \bar{x}_{n-1}\right|}{s_{n-1}} \tag{14}$$

where:
x_k, examined value, the result at the furthest distance from the mean
$\bar{x}_{n-1}$, the mean value of the population of the results with the examined result excluded
s_{n-1}, the standard deviation of the population of the results with the examined result excluded

- if *h* > critical value then reject x_k otherwise temporarily exclude the x_k from the population of results and proceed with testing the next outlier candidate, if the following value of *h* > critical value then reject both results, decrease *n* respectively, repeat the procedure until $h \le$ critical value.

4. Dixon's test [9], number of results: $3 \le n \le 25$, two-sided test, confidence level = 0.95:

- if x_1 is at the furthest distance from the mean value, then calculate:

$$r = \begin{cases} (x_2 - x_1)/(x_n - x_1), & 3 \le n \le 7 \\ (x_2 - x_1)/(x_{n-1} - x_1), & 8 \le n \le 10 \\ (x_3 - x_1)/(x_{n-1} - x_1), & 11 \le n \le 13 \\ (x_3 - x_1)/(x_{n-2} - x_1), & 14 \le n \le 25 \end{cases} \tag{15a}$$

- if x_n is at the furthest distance from the mean value then calculate:

$$r = \begin{cases} (x_n - x_{n-1})/(x_n - x_1), & 3 \le n \le 7 \\ (x_n - x_{n-1})/(x_n - x_2), & 8 \le n \le 10 \\ (x_n - x_{n-2})/(x_n - x_2), & 11 \le n \le 13 \\ (x_n - x_{n-2})/(x_n - x_3), & 14 \le n \le 25 \end{cases} \tag{15b}$$

- if $r >$ critical value then reject the tested result, decrease n, repeat the procedure until $r \leq$ critical value.

5. Outlier rejection test proposed in [6], number of results: $4 \leq n \leq 100$, two-sided test, confidence level = 0.95:

$$w/s = (x_n - x_1)/s \qquad (16)$$

- if $w/s >$ critical value then: if $x_n - \bar{x} = \bar{x} - x_1$, reject both x_1 and x_n, otherwise reject x_k ($x_k = x_1$ or $x_k = x_n$), the result that is at the furthest distance from the mean, for the remaining population of results ($n` = n - 1$) calculate: $T_k = |\bar{x}' - x_k| / s'$, where: $\bar{x}'$ is the mean value and s' is the standard deviation of the population of the results excluding the rejected value x_k, if $T_k >$ critical value then reject also the second extreme result, decrease n respectively, repeat the procedure until $w/s \leq$ critical value.

6. Outlier rejection test proposed in [10], number of results: $3 \leq n < \infty$, two-sided test, confidence level = 0.95:

$$B_4 = |x_k - \bar{x}| / s \qquad (17)$$

where:
x_k, examined value

- if $B_4 >$ critical value then reject the tested result, repeat the procedure until $B_4 \leq$ critical value.

7. Outlier rejection test proposed in [11], number of results: $3 \leq n \leq 100$, two-sided test, confidence level = 0.95:

$$S_k^2 / S = \frac{\sum_{i=1, i \neq k}^{n} (x_i - \bar{x}')^2}{\sum_{i=1, i \neq k}^{n} (x_i - \bar{x})^2}, \quad k = 1 \; or \; k = n \qquad (18)$$

where:
x_k, examined value, the result at the furthest distance from the mean
$\bar{x}'$, the mean value of the population of the results with the examined result x_k excluded

- if $S_k^2 / S >$ critical value then reject x_k, decrease n, repeat the procedure until $S_k^2 / S \leq$ critical value.

After outlier rejection procedure the remaining results were used to calculate the consensus mean value of analyte, X_C, and corresponding consensus value of its standard deviation, σ_C:

$$X_C = \frac{\sum_{i=1}^{m} x_i}{m} \quad (19)$$

and

$$\sigma_C = \sqrt{\frac{\sum_{i=1}^{m} (x_i - X_C)^2}{m(m-1)}} \quad (20)$$

The term m denotes the number of reported values for a given analyte excluding the outliers rejected by at least one of the outlier rejections tests. The summing up in Eqn. (19) and (20) takes into account only the results which passed all the outlier rejection tests. The obtained consensus values were compared with the assigned values of analytes.

RESULTS

The test material was distributed to 37 laboratories applying XRF technique for elemental analysis. Out of the 37 laboratories 22 have provided the required analytical results. The list of the participating laboratories is presented in Table 1. One of the laboratories did not report explicitly the uncertainties of analytical results. In this case it was assumed that the last significant digit of the reported result was a good estimate of its uncertainty. Although, only one analytical technique was used by all the participants (XRF), there were differences between laboratories due to different excitation-detection conditions applied in different XRF spectrometers. Therefore the reported results were classified accordingly as specified in Table 2. The participants provided 361 analytical results for 42 analytes out of which 325 results for 34 analytes have been evaluated. Besides the analytes for which the assigned values were known the participants reported also results for the following analytes: Al_2O_3, SiO_2, P_2O_5, Cl, Nb, Ag, Sn, Pr. These results were not evaluated in this proficiency test round. In Table 3 a summary of the assigned analyte values, the target values of standard deviation, as well as the consensus values are shown. The consensus values were calculated using Eqns. (19) and (20) based on 290 reported analytical results after excluding 35 results classified as outliers from the initial population of 325 results. The correlation between the assigned and the consensus values is shown in Fig. 2. As can be noticed there is a good overall agreement between the assigned and the consensus values, except for the isolated cases of Hg, Sb, S and MgO. These analytes were reported by single laboratories, except MgO, which was reported by 3 participants, therefore one could expect a biased consensus value. The remaining results correlated well with the assigned values of analytes, especially these related to the elements with the recommended concentrations in the IAEA-SL-1 reference material. Such a trend in the reported data confirms the reference material as a proper sample for the proficiency test exercise. In Table 4 the reported values are listed together with z-scores and u-scores calculated for the three different fit-for-purpose ranges, as defined in Eqn. (2). In Figs. 3 and 4 the distributions of the proficiency test results are shown. The data for analytes reported by at least 6 laboratories are presented in these graphs. In Fig. 3 the density distributions are presented. Due to rather low number of results, these graphs could only be used as indicators of the trends observed in the reported data. Some of the presented distributions show grouping of the results indicating possible bimodal distributions, as for CaO, Cu, Zn, Sr and Pb. As pointed out in Table 3, in a few cases the populations of the results for a given analyte did not pass the normality test (Kolmogorov-Smirnov test), however after rejecting the outliers all the tested populations passed the test. In

Fig. 4 the bar chart distributions of reported results are presented. The results are sorted in ascending order versus laboratory code and they are accompanied by technique codes marked on a linked upper *X*-axis. The decision levels $|z| < 2$ for different fit-for-purpose ranges have also been marked on the graphs. For every participating laboratory its overall performance is presented in Fig. 5. The graphs presented in this figure relate all the *u*-scores and *z*-scores calculated for a given laboratory. The decision limits marked with black lines ($|z| < 3$, $u < 3.29$) divide the plot area in four quadrants. Due to inequality (10) all the points lay always below the line $u = z$. The smaller the laboratory estimated uncertainty is the closer the related point lays to the $u = z$ line. The better performing laboratories would have more points located in the lower-left quadrant of the plot. If there are many points located in the upper-right quadrant it suggests that these results do not fall in the defined fit-for-purpose ranges and that the laboratory provided too "optimistic" uncertainty estimate which requires some care and revision. The participants are advised to examine in detail their results presented in Table 4, Figs. 4 and 5 in order to better define their fit-for-purpose status as well to identify the analytes or analyte groups requiring improvement in the analytical procedures.

The participants were also asked to report additional information about the analytical process, which included the data on technique applied, methods of sample preparation, algorithms used for X-ray spectra deconvolution (for EDXRFS) and algorithms applied to calculate the concentrations of analytes. The summary of the collected data is presented in Fig. 6. As can be noticed the majority of the determinations (above 76% of the reported results) were performed on samples prepared in the form of pressed pellets. X-ray tube excitation (about 58% of the reported results) was slightly in favor of radioisotope source excitation (42% of results). As the utilized software is concerned, for the X-ray spectra deconvolution the most frequently used software is the AXIL program (about 63%) which is included in the QXAS software package [12] and commercial software (about 30%) delivered together with the spectrometer. For quantitative analysis the preferences of laboratories are more equally spread between QAES program [13, 14] (about 31%), commercial software (about 30%) and QXAS software package (about 24%). Of course one has to remember that these percentages are based on data from only 22 laboratories, therefore they cannot be recognized as representative for the whole XRF laboratories community.

The authors of the proficiency test scheme are grateful to the participants for providing the additional information on the analytical process. It has to be emphasized that to really benefit from the proficiency testing a regular participation in the scheme is required. The laboratories are invited to take part in the next PTXRFIAEA/02 round which will be announced soon.

Acknowledgement

The XRF Group/Instrumentation Unit which carried out the proficiency test is grateful to the Colleagues from the Chemistry Unit, the IAEA Laboratories, Seibersdorf, Austria for their kind assistance and advice. In particular the authors of the report wish to express their appreciation to Mr. Zbigniew Radecki for sharing with us his expertise in statistical data evaluation and his useful suggestions concerning the presentation of the results.

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APPENDIX I

Tables 1-5

Table 1. The laboratories participating in the proficiency test exercise.

Analyst Name	Institution	Country
Nikolla Civici	Institute of Nuclear Physics, Tirana	**Albania**
Ivone Mulako Sato, Vera Lúcia R. Salvador	Cidade Universitária, Rua do Matão, São Paulo	**Brazil**
Dr. Ari Artinian	Bulgarian Academy of Sciences Institute for Nuclear Research and Nuclear Energy – BAS, Sofia	**Bulgaria**
Luis Ramon Portillo Trujillo	Centro de Investigaciones y Aplicaciones Nucleares (CIAN) Facultad de Ingenieria y Arquit Universidad de El Salvador, San. Salvador	**El Salvador**
Zoltán Szőkefalvi-Nagy	KFKI Research Institute for Particle and Nuclear Physics, Konkoly-Thege Miklós	**Hungary**
Michael J. Mangala	Institute of Nuclear Science, University of Nairobi, Nairobi	**Kenya**
Pr. Raoelina Andriambololona	Institut National des Sciences et Techniques Nucléaires (Madagascar-INSTN), Antananarivo	**Madagascar**
Soumana Salifou	Institut des Radio-isotopes, Niamey	**Niger**
Idris Isa Funtua	Centre for Energy Research and Training, Ahmadu Bello University, Zaria	**Nigeria**
Habib-ur-Rehman	SSO, CAFD, PINSTECH, P.O. Nilore, Islamabad	**Pakistan**
Paula Olivera	Dpto. Química - PRDT Instituto Peruano de Energía Nuclear, San Borja, Lima	**Peru**
Flora L. Santos	Philippine Nuclear Research Institute, Diliman, Quezon City	**Philippines**
M. Alexandra Barreiros	INETI / LAACQ, Lisboa	**Portugal**

Table 1 continued

Analyst Name	Institution	Country
Peter Kump	J. Stefan Institute, Ljubljana	**Slovenia**
M.C. Shirani Seneviratne	Atomic Energy Authority, Orugodawatte, Wellampitiya	**Sri Lanka**
Dr. Farouk Habbani	Department of Physics, Faculty of Science, University of Khartoum, Khartoun	**Sudan**
Haisam Issa	AECS, Damascus	**Syria**
Dr. Somporn Chongkum	Physics Division, Office of Atomic Energy for Peace, Chatuchak, Bangkok	**Thailand**
Dr. Sumpun Wongnawa	Department of Chemistry Faculty of Science Prince of Songkla University, Hat Yai , Songkla	**Thailand**
Dr. Phil Potts	Dept. of Earth Sciences, The Open University, Milton Keynes	**United Kingdom**
John S. Watson	Dept. of Earth Sciences, The Open University, Milton Keynes	**United Kingdom**
Dzengo Mzengeza	Institute of Mining Research University of Zimbabwe, Harare	**Zimbabwe**

Table 2. The coding, description and the abbreviated names of the X-ray fluorescence techniques used by participants of the proficiency test exercise.

Technique Code	Description	Abbreviation
1.0	Energy dispersive X-ray fluorescence spectrometry	EDXRFS
1.1	Energy dispersive X-ray fluorescence spectrometry, radioisotope excitation	EDXRFS-R
1.2	Energy dispersive X-ray fluorescence spectrometry, X-ray tube excitation	EDXRFS-T
1.3	Total reflection X-ray fluorescence spectrometry	TXRFS
2.0	Wavelength dispersive X-ray fluorescence Spectrometry	WDXRFS

Table 3. The assigned analyte values, the target values of the standard deviations and the consensus values calculated using the reported results. The concentrations of the analytes marked in bold are recommended in the IAEA-SL-1 report with relatively high or reasonable degree of confidence.

Analyte symbol	Assigned value of the analyte, X_A	Target value of standard deviation, σ_A			Consensus value of the analyte, X_C	Consensus value of the standard deviation, σ_C	Number of results	Number of outliers	Normality test*
		k = 0.5	k = 1.0	k = 1.5					
			[wt. %]						
Na_2O	0.232	0.006	0.012	0.017	0.203	0.029	3	0	-
MgO	4.886	0.077	0.154	0.231	1.311	0.323	3	0	-
S	1.178	0.023	0.046	0.069	0.071	0.007	3	1	-
K_2O	1.750	0.032	0.064	0.096	1.517	0.031	19	2	passed
CaO	0.347	0.008	0.016	0.024	0.419	0.022	19	1	passed
TiO_2	0.862	0.018	0.035	0.053	0.799	0.028	19	2	passed
MnO	0.447	0.010	0.020	0.030	0.453	0.002	18	7	failed
Fe_2O_3	9.635	0.137	0.274	0.411	9.219	0.195	21	2	passed
			[mg/kg]						
Sc	17.29	0.90	1.80	2.70	21.20	5.00	1	0	-
V	170.4	6.3	12.6	18.9	209.2	13.2	9	0	passed
Cr	103.7	4.1	8.3	12.4	105.8	5.6	10	3	failed
Co	19.83	1.01	2.02	3.04	18.25	7.75	3	1	-
Ni	44.92	2.03	4.05	6.08	39.32	3.25	12	2	failed
Cu	29.98	1.44	2.87	4.31	42.63	5.27	15	0	passed
Zn	223.0	7.9	15.8	23.7	220.5	6.0	19	2	passed
Ga	23.68	1.18	2.35	3.53	22.57	2.71	9	0	passed
As	27.59	1.34	2.68	4.02	29.41	2.91	10	1	failed
Se	2.850	0.195	0.389	0.584	2.65	2.90	1	0	-
Br	6.823	0.409	0.818	1.226	6.283	1.01	7	0	passed
Rb	113.1	4.4	8.9	13.3	112.6	6.2	18	0	passed
Sr	80.04	3.31	6.62	9.93	75.27	3.14	19	1	passed
Y	85.33	3.50	6.99	10.49	32.92	1.64	17	2	failed
Zr	240.6	8.4	16.9	25.3	166.0	4.8	17	3	passed
Mo	1.328	0.102	0.204	0.305	4.3	1.5	1	0	-
Sb	1.310	0.101	0.201	0.302	21.0	4.0	1	0	-
Cs	7.006	0.418	0.836	1.254	9.0	3.0	1	0	-
Ba	639.2	19.3	38.7	58.0	663.8	45.3	10	0	passed
La	52.62	2.32	4.64	6.95	38.00	3.06	5	2	-
Ce	116.6	4.6	9.1	13.7	88.67	2.03	4	1	-
Nd	43.78	1.98	3.97	5.95	28.17	10.66	4	1	-
Hg	0.130	0.014	0.028	0.042	31.4	3.14	1	0	-
Pb	37.73	1.75	3.50	5.24	46.08	5.37	17	1	failed
Th	13.98	0.75	1.50	2.26	13.11	0.91	7	0	passed
U	4.021	0.261	0.522	0.783	3.80	0.80	2	0	-

*- the populations with at least 6 reported results were tested using Kolmogorov-Smirnov test before outlier rejection procedures (after rejecting the outliers all examined populations passed the test).

Table 4. Summary of the reported results and the calculated z-scores and *u*-scores. The results rejected by at least one of the outlier rejection tests were marked with '*' in the analyte concentration column.

Laboratory code	Technique code	Analyte concentration	Standard dev.	Relative std. dev., [%]	*z*-scores			*u*-scores		
					$k = 0.5$	$k = 1.0$	$k = 1.5$	$k = 0.5$	$k = 1.0$	$k = 1.5$
					Na_2O [wt. %]					
6	2.0	0.16	0.01	6.25	-12.46	-6.23	-4.15	6.23	4.71	3.60
3	2.0	0.19	0.024	12.63	-7.27	-3.63	-2.42	1.70	1.58	1.42
8	2.0	0.258	0.001	0.39	4.50	2.25	1.50	4.43	2.24	1.50
					MgO [wt. %]					
3	2.0	0.91	0.027	2.97	-51.66	-25.83	-17.22	48.75	25.44	17.10
8	2.0	1.074	0.001	0.09	-49.53	-24.77	-16.51	49.53	24.77	16.51
6	2.0	1.95	0.05	2.56	-38.15	-19.07	-12.72	31.99	18.14	12.43
					S [wt. %]					
3	2.0	0.063	0.0035	5.55	-48.51	-24.25	-16.17	47.95	24.18	16.15
15	1.1	0.078	0.02	25.64	-47.86	-23.93	-15.95	36.10	21.94	15.32
21	1.2	1.12*	0.96	85.71	-2.52	-1.26	-0.84	0.06	0.06	0.06
					K_2O [wt. %]					
1	1.1	0.912*	0.047	5.15	-26.05	-13.03	-8.68	14.72	10.52	7.81
6	2.0	1.16*	0.01	0.86	-18.34	-9.17	-6.11	17.51	9.06	6.08
21	1.2	1.2	0.11	9.17	-17.10	-8.55	-5.70	4.80	4.32	3.76
3	2.0	1.34	0.024	1.79	-12.74	-6.37	-4.25	10.22	5.97	4.12
12	1.2	1.36	0.1	7.35	-12.12	-6.06	-4.04	3.71	3.28	2.81
10	1.0	1.45	0.09	6.21	-9.33	-4.66	-3.11	3.14	2.71	2.27
14	1.1	1.45	0.03	2.07	-9.33	-4.66	-3.11	6.82	4.23	2.97
11	1.1	1.48	0.23	15.54	-8.39	-4.20	-2.80	1.16	1.13	1.08
22	2.0	1.506	0.1084	7.20	-7.59	-3.80	-2.53	2.16	1.94	1.68
2	1.3	1.507	0.1156	7.67	-7.55	-3.78	-2.52	2.03	1.84	1.61
4	1.1	1.554	0.1554	10.00	-6.10	-3.05	-2.03	1.24	1.17	1.07
16	1.3	1.576	0.0173	1.10	-5.40	-2.70	-1.80	4.75	2.61	1.77
8	2.0	1.579	0.001	0.06	-5.32	-2.66	-1.77	5.31	2.66	1.77
7	1.1	1.579	0.205	12.98	-5.32	-2.66	-1.77	0.82	0.80	0.75
9	1.0	1.58	0.3	18.99	-5.28	-2.64	-1.76	0.56	0.55	0.54
20	1.1	1.59	0.13	8.18	-4.97	-2.49	-1.66	1.20	1.10	0.99
13	1.1	1.633	0.1252	7.66	-3.63	-1.82	-1.21	0.90	0.83	0.74
15	1.1	1.69	0.18	10.65	-1.87	-0.93	-0.62	0.33	0.31	0.29
5	1.2	1.71	0.16	9.36	-1.24	-0.62	-0.41	0.25	0.23	0.21
					CaO [wt. %]					
19	1.0	0.102*	0.001	0.98	-30.11	-15.05	-10.04	29.88	15.02	10.03
1	1.1	0.246	0.013	5.12	-12.41	-6.21	-4.14	6.73	4.91	3.68
5	1.2	0.30	0.03	10.00	-5.78	-2.89	-1.93	1.51	1.38	1.22
21	1.2	0.34	0.04	11.76	-0.86	-0.43	-0.29	0.17	0.16	0.15
22	2.0	0.35	0.014	4.00	0.34	0.17	0.11	0.17	0.13	0.10
13	1.1	0.357	0.0874	24.47	1.27	0.64	0.42	0.12	0.12	0.11

Table 4 continued…

Laboratory code	Technique code	Analyte concentration	Standard dev.	Relative std. dev., [%]	z-scores $k = 0.5$	z-scores $k = 1.0$	z-scores $k = 1.5$	u-scores $k = 0.5$	u-scores $k = 1.0$	u-scores $k = 1.5$
14	1.1	0.36	0.01	2.78	1.60	0.80	0.53	1.01	0.68	0.49
3	2.0	0.38	0.013	3.42	4.06	2.03	1.35	2.15	1.58	1.19
12	1.2	0.4	0.03	7.50	6.51	3.26	2.17	1.71	1.55	1.37
7	1.1	0.406	0.098	24.14	7.25	3.63	2.42	0.60	0.59	0.58
16	1.3	0.426	0.0084	1.96	9.75	4.87	3.25	6.79	4.33	3.07
20	1.1	0.43	0.06	13.95	10.20	5.10	3.40	1.37	1.34	1.28
8	2.0	0.446	0.001	0.22	12.17	6.08	4.06	12.07	6.07	4.05
15	1.1	0.45	0.15	33.33	12.66	6.33	4.22	0.69	0.68	0.68
2	1.3	0.465	0.049	10.54	14.44	7.22	4.82	2.37	2.28	2.15
10	1.0	0.481	0.032	6.65	16.47	8.23	5.49	4.06	3.73	3.33
6	2.0	0.53	0.01	1.89	22.49	11.24	7.50	14.19	9.58	6.94
4	1.1	0.532	0.0532	10.00	22.70	11.35	7.57	3.43	3.32	3.16
11	1.1	0.64	0.01	1.56	36.00	18.00	12.00	22.73	15.34	11.11
					TiO_2 [wt. %]					
19	1.0	0.24*	0.01	4.17	-35.29	-17.65	-11.76	30.70	16.98	11.56
1	1.1	0.297*	0.005	1.68	-32.07	-16.03	-10.69	30.85	15.87	10.64
14	1.1	0.57	0.03	5.26	-16.58	-8.29	-5.53	8.40	6.32	4.81
16	1.3	0.62	0.0068	1.09	-13.73	-6.87	-4.58	12.82	6.74	4.54
11	1.1	0.68	0.03	4.41	-10.34	-5.17	-3.45	5.24	3.94	3.00
21	1.2	0.71	0.05	7.04	-8.64	-4.32	-2.88	2.87	2.49	2.09
10	1.0	0.72	0.04	5.56	-8.08	-4.04	-2.69	3.26	2.67	2.15
2	1.3	0.766	0.0167	2.18	-5.49	-2.74	-1.83	3.99	2.48	1.74
12	1.2	0.77	0.05	6.49	-5.24	-2.62	-1.75	1.74	1.51	1.27
13	1.1	0.787	0.0482	6.13	-4.29	-2.14	-1.43	1.47	1.27	1.06
15	1.1	0.8	0.09	11.25	-3.54	-1.77	-1.18	0.68	0.65	0.60
5	1.2	0.83	0.02	2.41	-1.84	-0.92	-0.61	1.22	0.80	0.57
8	2.0	0.838	0.001	0.12	-1.38	-0.69	-0.46	1.38	0.69	0.46
22	2.0	0.851	0.0334	3.92	-0.66	-0.33	-0.22	0.31	0.24	0.19
7	1.1	0.883	0.068	7.70	1.17	0.58	0.39	0.29	0.27	0.24
3	2.0	0.9	0.016	1.78	2.13	1.07	0.71	1.58	0.97	0.68
4	1.1	0.934	0.0934	10.00	4.07	2.03	1.36	0.75	0.72	0.67
9	1.0	0.94	0.16	17.02	4.40	2.20	1.47	0.48	0.47	0.46
6	2.0	0.99	0.01	1.01	7.24	3.62	2.41	6.29	3.48	2.37
					MnO [wt. %]					
14	1.1	0.27*	0.02	7.41	-17.53	-8.76	-5.84	7.89	6.22	4.87
16	1.3	0.36*	0.0034	0.93	-8.57	-4.29	-2.86	8.13	4.23	2.84
11	1.1	0.41*	0.01	2.44	-3.65	-1.82	-1.22	2.59	1.63	1.16
12	1.2	0.431*	0.028	6.50	-1.57	-0.78	-0.52	0.53	0.46	0.38
2	1.3	0.444	0.0207	4.65	-0.26	-0.13	-0.09	0.11	0.09	0.07
22	2.0	0.448	0.0116	2.59	0.13	0.06	0.04	0.08	0.06	0.04
5	1.2	0.45	0.01	2.22	0.32	0.16	0.11	0.23	0.14	0.10
3	2.0	0.45	0.011	2.44	0.32	0.16	0.11	0.21	0.14	0.10
15	1.1	0.45	0.1	22.22	0.32	0.16	0.11	0.03	0.03	0.03
7	1.1	0.452	0.039	8.63	0.52	0.26	0.17	0.13	0.12	0.11
8	2.0	0.453	0.001	0.22	0.61	0.31	0.20	0.61	0.31	0.20
13	1.1	0.454	0.0119	2.62	0.74	0.37	0.25	0.48	0.32	0.23
21	1.2	0.46	0.03	6.52	1.31	0.65	0.44	0.42	0.37	0.31

Table 4 continued…

Laboratory code	Technique code	Analyte concentration	Standard dev.	Relative std. dev., [%]	z-scores $k = 0.5$	z-scores $k = 1.0$	z-scores $k = 1.5$	u-scores $k = 0.5$	u-scores $k = 1.0$	u-scores $k = 1.5$
20	1.1	0.46	0.02	4.35	1.31	0.65	0.44	0.59	0.46	0.36
4	1.1	0.465	0.0465	10.00	1.79	0.89	0.60	0.38	0.36	0.33
9	1.0	0.54*	0.12	22.22	9.24	4.62	3.08	0.77	0.77	0.75
6	2.0	0.58*	0.01	1.72	13.20	6.60	4.40	9.38	5.92	4.18
1	1.1	0.898*	0.0715	7.97	44.70	22.35	14.90	6.24	6.07	5.81
					Fe_2O_3 [wt. %]					
19	1.0	2.752*	0.001	0.04	-50.23	-25.12	-16.74	50.23	25.12	16.74
14	1.1	7.63	0.08	1.05	-14.63	-7.32	-4.88	12.64	7.02	4.79
4	1.1	7.635	0.7635	10.00	-14.60	-7.30	-4.87	2.58	2.47	2.31
16	1.3	7.883	0.0176	0.22	-12.78	-6.39	-4.26	12.68	6.38	4.26
9	1.0	8.6	2.66	30.93	-7.55	-3.78	-2.52	0.39	0.39	0.38
21	1.2	8.78	0.65	7.40	-6.24	-3.12	-2.08	1.29	1.21	1.11
12	1.2	8.89	0.51	5.74	-5.44	-2.72	-1.81	1.41	1.29	1.14
10	1.0	9	0.54	6.00	-4.63	-2.32	-1.55	1.14	1.05	0.94
2	1.3	9.207	0.4003	4.35	-3.12	-1.56	-1.04	1.01	0.88	0.75
11	1.1	9.27	0.58	6.26	-2.66	-1.33	-0.89	0.61	0.57	0.51
7	1.1	9.359	0.658	7.03	-2.01	-1.01	-0.67	0.41	0.39	0.36
20	1.1	9.37	0.36	3.84	-1.93	-0.97	-0.64	0.69	0.59	0.48
5	1.2	9.4	0.1	1.06	-1.71	-0.86	-0.57	1.39	0.81	0.56
22	2.0	9.593	0.2288	2.38	-0.30	-0.15	-0.10	0.16	0.12	0.09
13	1.1	9.651	0.1658	1.72	0.12	0.06	0.04	0.08	0.05	0.04
15	1.1	9.82	0.9	9.16	1.35	0.68	0.45	0.20	0.20	0.19
17	1.0	9.952	0.233	2.34	2.32	1.16	0.77	1.17	0.88	0.67
1	1.1	10.117	0.2145	2.12	3.52	1.76	1.17	1.89	1.39	1.04
8	2.0	10.38	0.01	0.10	5.44	2.72	1.81	5.42	2.72	1.81
3	2.0	10.63	0.048	0.45	7.26	3.63	2.42	6.85	3.58	2.41
6	2.0	13.75*	0.01	0.07	30.03	15.02	10.01	29.95	15.01	10.01
					Sc [mg/kg]					
8	2.0	21.2	5	23.58	4.34	2.17	1.45	0.77	0.74	0.69
					V [mg/kg]					
2	1.3	159	18	11.32	-1.82	-0.91	-0.61	0.60	0.52	0.44
12	1.2	165	50	30.30	-0.87	-0.43	-0.29	0.11	0.11	0.10
3	2.0	176	25	14.20	0.88	0.44	0.29	0.22	0.20	0.18
16	1.3	200.18	54.7	27.33	4.73	2.36	1.58	0.54	0.53	0.51
8	2.0	201	5	2.49	4.86	2.43	1.62	3.80	2.26	1.57
6	2.0	215	10	4.65	7.08	3.54	2.36	3.77	2.77	2.09
15	1.1	240	60	25.00	11.06	5.53	3.69	1.15	1.14	1.11
21	1.2	256	44.4	17.34	13.60	6.80	4.53	1.91	1.85	1.77
10	1.0	270.25	25.68	9.50	15.86	7.93	5.29	3.78	3.49	3.13
					Cr [mg/kg]					
6	2.0	45*	2	4.44	-14.24	-7.12	-4.75	12.81	6.92	4.68
2	1.3	85.8	9.8	11.42	-4.35	-2.17	-1.45	1.69	1.40	1.14
12	1.2	92	32	34.78	-2.84	-1.42	-0.95	0.36	0.36	0.34
3	2.0	103	26	25.24	-0.18	-0.09	-0.06	0.03	0.03	0.03
15	1.1	104	15	14.42	0.06	0.03	0.02	0.02	0.02	0.01

Table 4 continued…

Laboratory code	Technique code	Analyte concentration	Standard dev.	Relative std. dev., [%]	z-scores $k = 0.5$	z-scores $k = 1.0$	z-scores $k = 1.5$	u-scores $k = 0.5$	u-scores $k = 1.0$	u-scores $k = 1.5$
22	2.0	108	7.5	6.94	1.03	0.52	0.34	0.50	0.38	0.29
5	1.2	119	12	10.08	3.70	1.85	1.23	1.20	1.05	0.89
8	2.0	128.5	4	3.11	6.00	3.00	2.00	4.31	2.70	1.90
16	1.3	226.46*	50.16	22.15	29.74	14.87	9.92	2.44	2.41	2.38
21	1.2	324*	32.6	10.06	53.39	26.69	17.80	6.70	6.55	6.32
					Co [mg/kg]					
8	2.0	10.5	2	19.05	-9.22	-4.61	-3.08	4.16	3.28	2.57
6	2.0	26	1	3.85	6.09	3.05	2.03	4.33	2.73	1.93
18	1.3	336.8*	45.6	13.54	313.20	156.60	104.40	6.95	6.94	6.94
					Ni [mg/kg]					
6	2.0	18	1	5.56	-13.28	-6.64	-4.43	11.91	6.45	4.37
2	1.3	25.6	3.4	13.28	-9.53	-4.77	-3.18	4.88	3.65	2.77
15	1.1	37	10	27.03	-3.91	-1.96	-1.30	0.78	0.73	0.68
20	1.1	39.5	9	22.78	-2.68	-1.34	-0.89	0.59	0.55	0.50
21	1.2	41.8	5.62	13.44	-1.54	-0.77	-0.51	0.52	0.45	0.38
3	2.0	43	20	46.51	-0.95	-0.47	-0.32	0.10	0.09	0.09
22	2.0	43.7	2.2	5.03	-0.60	-0.30	-0.20	0.41	0.27	0.19
12	1.2	44	5	11.36	-0.46	-0.23	-0.15	0.17	0.14	0.12
1	1.1	50	5	10.00	2.51	1.25	0.84	0.94	0.79	0.65
8	2.0	50.6	3	5.93	2.80	1.40	0.93	1.57	1.13	0.84
5	1.2	71.1*	5	7.03	12.92	6.46	4.31	4.85	4.07	3.33
17	1.0	113.07*	44.28	39.16	33.63	16.81	11.21	1.54	1.53	1.53
					Cu [mg/kg]					
1	1.1	10	2	20.00	-13.90	-6.95	-4.63	8.11	5.71	4.20
11	1.1	12.9	4.1	31.78	-11.88	-5.94	-3.96	3.93	3.41	2.87
2	1.3	24.5	2.3	9.39	-3.81	-1.91	-1.27	2.02	1.49	1.12
12	1.2	30	5.8	19.33	0.01	0.01	0.00	0.00	0.00	0.00
8	2.0	30.7	3	9.77	0.50	0.25	0.17	0.22	0.17	0.14
20	1.1	33	3	9.09	2.10	1.05	0.70	0.91	0.73	0.58
15	1.1	33	5	15.15	2.10	1.05	0.70	0.58	0.52	0.46
17	1.0	44.98	23.62	52.51	10.44	5.22	3.48	0.63	0.63	0.62
6	2.0	48	2	4.17	12.54	6.27	4.18	7.32	5.15	3.79
14	1.1	50	30	60.00	13.93	6.97	4.64	0.67	0.66	0.66
4	1.1	51.5	5.15	10.00	14.97	7.49	4.99	4.03	3.65	3.20
5	1.2	56	3.5	6.25	18.10	9.05	6.04	6.88	5.75	4.69
10	1.0	63.9	12.5	19.56	23.60	11.80	7.87	2.70	2.65	2.57
3	2.0	68	19	27.94	26.45	13.23	8.82	2.00	1.98	1.95
9	1.0	83	16	19.28	36.89	18.44	12.30	3.30	3.26	3.20
					Zn [mg/kg]					
4	1.1	108*	10.8	10.00	-14.55	-7.28	-4.85	8.59	6.01	4.41
1	1.1	164	22	13.41	-7.47	-3.73	-2.49	2.53	2.18	1.83
21	1.2	194	15.2	7.84	-3.67	-1.84	-1.22	1.69	1.32	1.03
16	1.3	200.25	13.18	6.58	-2.88	-1.44	-0.96	1.48	1.11	0.84
12	1.2	201	12.5	6.22	-2.79	-1.39	-0.93	1.49	1.09	0.82
8	2.0	201	3	1.49	-2.79	-1.39	-0.93	2.61	1.37	0.92

Table 4 continued…

Laboratory code	Technique code	Analyte concentration	Standard dev.	Relative std. dev., [%]	z-scores k = 0.5	z-scores k = 1.0	z-scores k = 1.5	u-scores k = 0.5	u-scores k = 1.0	u-scores k = 1.5
10	1.0	209	18.36	8.78	-1.77	-0.89	-0.59	0.70	0.58	0.47
11	1.1	215	17	7.91	-1.02	-0.51	-0.34	0.43	0.35	0.28
2	1.3	215.4	8.4	3.90	-0.96	-0.48	-0.32	0.66	0.43	0.30
15	1.1	217	23	10.60	-0.76	-0.38	-0.25	0.25	0.22	0.18
7	1.1	223	17.3	7.76	0.00	0.00	0.00	0.00	0.00	0.00
22	2.0	234	10	4.27	1.39	0.69	0.46	0.86	0.59	0.43
3	2.0	234	21	8.97	1.39	0.69	0.46	0.49	0.42	0.35
6	2.0	240	3	1.25	2.15	1.07	0.72	2.01	1.06	0.71
20	1.1	241	11	4.56	2.27	1.14	0.76	1.33	0.93	0.69
9	1.0	247	41	16.60	3.03	1.52	1.01	0.57	0.55	0.51
13	1.1	254	10	3.94	3.92	1.96	1.31	2.43	1.66	1.20
14	1.1	258	38	14.73	4.42	2.21	1.48	0.90	0.85	0.78
5	1.2	323*	17	5.26	12.65	6.32	4.22	5.33	4.31	3.43
					Ga [mg/kg]					
18	1.3	10	1.35	13.50	-11.63	-5.82	-3.88	7.64	5.04	3.62
10	1.0	15.6	0.1	0.64	-6.87	-3.44	-2.29	6.85	3.43	2.29
21	1.2	17	2.28	13.41	-5.68	-2.84	-1.89	2.61	2.04	1.59
11	1.1	21.5	5.2	24.19	-1.86	-0.93	-0.62	0.41	0.38	0.35
20	1.1	22	3	13.64	-1.43	-0.72	-0.48	0.52	0.44	0.36
12	1.2	23	2.5	10.87	-0.58	-0.29	-0.19	0.25	0.20	0.16
15	1.1	25	4	16.00	1.12	0.56	0.37	0.32	0.28	0.25
3	2.0	34	15	44.12	8.77	4.39	2.92	0.69	0.68	0.67
6	2.0	35	2	5.71	9.62	4.81	3.21	4.88	3.67	2.79
					As [mg/kg]					
1	1.1	17	12	70.59	-7.91	-3.95	-2.64	0.88	0.86	0.84
21	1.2	17.2	3.69	21.45	-7.76	-3.88	-2.59	2.65	2.28	1.90
20	1.1	28	3	10.71	0.31	0.15	0.10	0.13	0.10	0.08
7	1.1	28.5	7.4	25.96	0.68	0.34	0.23	0.12	0.12	0.11
12	1.2	29	4.8	16.55	1.05	0.53	0.35	0.28	0.26	0.23
8	2.0	30.5	5	16.39	2.17	1.09	0.72	0.56	0.51	0.45
2	1.3	31.5	2.8	8.89	2.92	1.46	0.97	1.26	1.01	0.80
15	1.1	40	7	17.50	9.27	4.63	3.09	1.74	1.66	1.54
10	1.0	43.03	9.67	22.47	11.53	5.77	3.84	1.58	1.54	1.48
6	2.0	75*	5	6.67	35.40	17.70	11.80	9.16	8.36	7.39
					Se [mg/kg]					
21	1.2	2.65	2.897	109.32	-1.03	-0.51	-0.34	0.07	0.07	0.07
					Br [mg/kg]					
21	1.2	2.88	3.73	129.51	-9.65	-4.82	-3.22	1.05	1.03	1.00
12	1.2	4.5	1.2	26.67	-5.68	-2.84	-1.89	1.83	1.60	1.35
15	1.1	5	3	60.00	-4.46	-2.23	-1.49	0.60	0.59	0.56
6	2.0	6	1	16.67	-2.01	-1.01	-0.67	0.76	0.64	0.52
1	1.1	7	2	28.57	0.43	0.22	0.14	0.09	0.08	0.08
11	1.1	7.4	1.8	24.32	1.41	0.71	0.47	0.31	0.29	0.26
20	1.1	11.2	1.3	11.61	10.71	5.35	3.57	3.21	2.85	2.45

Table 4 continued…

Laboratory code	Technique code	Analyte concentration	Standard dev.	Relative std. dev., [%]	z-scores $k = 0.5$	z-scores $k = 1.0$	z-scores $k = 1.5$	u-scores $k = 0.5$	u-scores $k = 1.0$	u-scores $k = 1.5$
					Rb [mg/kg]					
4	1.1	60.8	6.08	10.00	-11.78	-5.89	-3.93	6.95	4.86	3.57
3	2.0	79	9	11.39	-7.68	-3.84	-2.56	3.40	2.70	2.12
21	1.2	81.4	6.26	7.69	-7.14	-3.57	-2.38	4.13	2.92	2.15
10	1.0	90.26	6.26	6.94	-5.14	-2.57	-1.71	2.98	2.10	1.55
5	1.2	100	2	2.00	-2.95	-1.47	-0.98	2.69	1.44	0.97
12	1.2	101	6.1	6.04	-2.72	-1.36	-0.91	1.60	1.12	0.83
16	1.3	103.88	7.38	7.10	-2.08	-1.04	-0.69	1.07	0.80	0.60
8	2.0	109.1	2	1.83	-0.90	-0.45	-0.30	0.82	0.44	0.30
11	1.1	111	6	5.41	-0.47	-0.24	-0.16	0.28	0.20	0.14
13	1.1	115	2	1.74	0.43	0.21	0.14	0.39	0.21	0.14
20	1.1	116	5	4.31	0.65	0.33	0.22	0.43	0.29	0.20
15	1.1	117	12	10.26	0.88	0.44	0.29	0.31	0.26	0.22
7	1.1	118.5	2.9	2.45	1.22	0.61	0.41	1.02	0.58	0.40
14	1.1	124	9	7.26	2.46	1.23	0.82	1.09	0.86	0.68
2	1.3	135	18	13.33	4.93	2.47	1.65	1.18	1.09	0.98
6	2.0	149	2	1.34	8.09	4.04	2.70	7.37	3.95	2.67
1	1.1	150	14	9.33	8.31	4.16	2.77	2.51	2.23	1.91
9	1.0	166	30	18.07	11.92	5.96	3.97	1.75	1.69	1.61
					Sr [mg/kg]					
4	1.1	47.2	4.72	10.00	-9.92	-4.96	-3.31	5.70	4.04	2.99
21	1.2	56.3	4.41	7.83	-7.17	-3.59	-2.39	4.31	2.98	2.19
22	2.0	62	23	37.10	-5.45	-2.72	-1.82	0.78	0.75	0.72
10	1.0	65.26	4.65	7.13	-4.46	-2.23	-1.49	2.59	1.83	1.35
16	1.3	66.68	7.8	11.70	-4.04	-2.02	-1.35	1.58	1.31	1.06
5	1.2	70	2	2.86	-3.03	-1.52	-1.01	2.60	1.45	0.99
12	1.2	72	4.3	5.97	-2.43	-1.21	-0.81	1.48	1.02	0.74
11	1.1	72.1	2.3	3.19	-2.40	-1.20	-0.80	1.97	1.13	0.78
8	2.0	74.7	2	2.68	-1.61	-0.81	-0.54	1.38	0.77	0.53
15	1.1	77	8	10.39	-0.92	-0.46	-0.31	0.35	0.29	0.24
7	1.1	80.7	2.5	3.10	0.20	0.10	0.07	0.16	0.09	0.06
20	1.1	81	3	3.70	0.29	0.15	0.10	0.22	0.13	0.09
3	2.0	81	12	14.81	0.29	0.15	0.10	0.08	0.07	0.06
13	1.1	82	2	2.44	0.59	0.30	0.20	0.51	0.28	0.19
1	1.1	83	7	8.43	0.90	0.45	0.30	0.38	0.31	0.24
2	1.3	90	12	13.33	3.01	1.51	1.00	0.80	0.73	0.64
14	1.1	90	7	7.78	3.01	1.51	1.00	1.29	1.03	0.82
6	2.0	104	2	1.92	7.24	3.62	2.41	6.20	3.47	2.37
9	1.0	120*	25	20.83	12.07	6.04	4.02	1.59	1.55	1.49
					Y [mg/kg]					
21	1.2	18.2	1.83	10.05	-19.21	-9.60	-6.40	17.02	9.29	6.31
4	1.1	23.2	2.32	10.00	-17.78	-8.89	-5.93	14.81	8.44	5.79
2	1.3	27.8	3.9	14.03	-16.46	-8.23	-5.49	10.99	7.19	5.14
10	1.0	30.16	2.64	8.75	-15.78	-7.89	-5.26	12.60	7.38	5.10
11	1.1	31.6	2.1	6.65	-15.37	-7.69	-5.12	13.18	7.36	5.03
9	1.0	32	9	28.13	-15.26	-7.63	-5.09	5.52	4.68	3.86

Table 4 continued…

Laboratory code	Technique code	Analyte concentration	Standard dev.	Relative std. dev., [%]	z-scores			u-scores		
					k = 0.5	k = 1.0	k = 1.5	k = 0.5	k = 1.0	k = 1.5
20	1.1	33	2	6.06	-14.97	-7.49	-4.99	13.00	7.20	4.90
12	1.2	34	2.1	6.18	-14.69	-7.34	-4.90	12.59	7.03	4.80
5	1.2	34	1	2.94	-14.69	-7.34	-4.90	14.12	7.27	4.87
14	1.1	35	5	14.29	-14.40	-7.20	-4.80	8.25	5.86	4.33
15	1.1	36	4	11.11	-14.11	-7.06	-4.71	9.29	6.13	4.40
8	2.0	38.1	2	5.25	-13.51	-6.76	-4.50	11.73	6.50	4.43
7	1.1	38.8	2.1	5.41	-13.31	-6.66	-4.44	11.41	6.38	4.35
1	1.1	39	7	17.95	-13.26	-6.63	-4.42	5.92	4.68	3.68
3	2.0	43	12	27.91	-12.11	-6.06	-4.04	3.39	3.05	2.66
13	1.1	86*	1	1.16	0.19	0.10	0.06	0.18	0.09	0.06
6	2.0	90*	2	2.22	1.34	0.67	0.45	1.16	0.64	0.44
					Zr [mg/kg]					
4	1.1	92.2*	9.22	10.00	-17.60	-8.80	-5.87	11.88	7.72	5.51
10	1.0	134.3	8.54	6.36	-12.61	-6.30	-4.20	8.86	5.62	3.98
5	1.2	143	3	2.10	-11.58	-5.79	-3.86	10.91	5.70	3.83
12	1.2	145	11	7.59	-11.34	-5.67	-3.78	6.90	4.75	3.47
2	1.3	149	10	6.71	-10.86	-5.43	-3.62	7.00	4.67	3.37
8	2.0	163.2	2	1.23	-9.18	-4.59	-3.06	8.93	4.56	3.05
15	1.1	166	17	10.24	-8.85	-4.42	-2.95	3.93	3.12	2.45
1	1.1	167	6	3.59	-8.73	-4.37	-2.91	7.11	4.11	2.83
3	2.0	168	14	8.33	-8.61	-4.31	-2.87	4.44	3.31	2.51
11	1.1	172	10	5.81	-8.14	-4.07	-2.71	5.25	3.50	2.52
7	1.1	172	2.6	1.51	-8.14	-4.07	-2.71	7.78	4.02	2.70
14	1.1	175	7	4.00	-7.78	-3.89	-2.59	5.99	3.59	2.50
20	1.1	182	8	4.40	-6.95	-3.48	-2.32	5.04	3.14	2.21
22	2.0	188	18	9.57	-6.24	-3.12	-2.08	2.65	2.13	1.70
6	2.0	199	2	1.01	-4.94	-2.47	-1.65	4.80	2.45	1.64
13	1.1	240*	2	0.83	-0.07	-0.04	-0.02	0.07	0.04	0.02
9	1.0	259*	59	22.78	2.18	1.09	0.73	0.31	0.30	0.29
					Mo [mg/kg]					
7	1.1	4.3	1.5	34.88	29.20	14.60	9.73	1.98	1.96	1.94
					Sb [mg/kg]					
15	1.1	21	4	19.05	195.70	97.86	65.24	4.92	4.92	4.91
					Cs [mg/kg]					
15	1.1	9	3	33.33	4.77	2.39	1.59	0.66	0.64	0.61
					Ba [mg/kg]					
2	1.3	462	76	16.45	-9.16	-4.58	-3.05	2.26	2.08	1.85
18	1.3	524.8	110	20.96	-5.91	-2.96	-1.97	1.02	0.98	0.92
15	1.1	530	60	11.32	-5.65	-2.82	-1.88	1.73	1.53	1.31
16	1.3	571.95	87.02	15.21	-3.48	-1.74	-1.16	0.75	0.71	0.64
12	1.1	621	18.5	2.98	-0.94	-0.47	-0.31	0.68	0.42	0.30
22	2.0	690	36	5.22	2.63	1.32	0.88	1.24	0.96	0.74
3	2.0	725	120	16.55	4.44	2.22	1.48	0.71	0.68	0.64

Table 4 continued…

Laboratory code	Technique code	Analyte concentration	Standard dev.	Relative std. dev., [%]	z-scores k = 0.5	z-scores k = 1.0	z-scores k = 1.5	u-scores k = 0.5	u-scores k = 1.0	u-scores k = 1.5
1	1.1	814	12	1.47	9.04	4.52	3.01	7.68	4.32	2.95
8	2.0	843.3	12	1.42	10.56	5.28	3.52	8.97	5.04	3.45
14	1.1	856	40	4.67	11.21	5.61	3.74	4.88	3.90	3.08
La [mg/kg]										
6	2.0	2.8*	0.1	3.57	-21.49	-10.75	-7.16	21.47	10.74	7.16
1	1.1	8*	1	12.50	-19.25	-9.63	-6.42	17.68	9.41	6.35
15	1.1	34	5	14.71	-8.03	-4.02	-2.68	3.38	2.73	2.17
14	1.1	36	25	69.44	-7.17	-3.59	-2.39	0.66	0.65	0.64
12	1.1	44	3.4	7.73	-3.72	-1.86	-1.24	2.10	1.50	1.11
Ce [mg/kg]										
15	1.1	85	9	10.59	-6.93	-3.47	-2.31	3.13	2.47	1.93
1	1.1	89	8	8.99	-6.06	-3.03	-2.02	3.00	2.28	1.74
12	1.1	92	4.5	4.89	-5.40	-2.70	-1.80	3.84	2.42	1.71
14	1.1	138*	70	50.72	4.70	2.35	1.57	0.31	0.30	0.30
Nd [mg/kg]										
6	2.0	7.5	0.1	1.33	-18.30	-9.15	-6.10	18.27	9.15	6.10
15	1.1	34	5	14.71	-4.93	-2.47	-1.64	1.82	1.53	1.26
12	1.1	43	3.8	8.84	-0.39	-0.20	-0.13	0.18	0.14	0.11
16	1.3	111.49*	28.12	25.22	34.16	17.08	11.39	2.40	2.38	2.36
Hg [mg/kg]										
4	1.1	31.4	3.14	10.00	2212.00	1106.00	737.40	9.96	9.96	9.96
Pb [mg/kg]										
6	2.0	2.3	0.1	4.35	-20.28	-10.14	-6.76	20.24	10.13	6.76
15	1.1	17	6	35.29	-11.86	-5.93	-3.96	3.32	2.99	2.60
2	1.3	27.6	3.3	11.96	-5.80	-2.90	-1.93	2.71	2.11	1.64
12	1.2	30	7.3	24.33	-4.43	-2.21	-1.48	1.03	0.96	0.86
8	2.0	36.3	5	13.77	-0.82	-0.41	-0.27	0.27	0.23	0.20
13	1.1	40	7	17.50	1.30	0.65	0.43	0.31	0.29	0.26
20	1.1	42	4	9.52	2.44	1.22	0.81	0.98	0.80	0.65
11	1.1	42.1	3.5	8.31	2.50	1.25	0.83	1.12	0.88	0.69
7	1.1	47.5	10.6	22.32	5.59	2.80	1.86	0.91	0.88	0.83
5	1.2	50.5	3.6	7.13	7.31	3.65	2.44	3.19	2.55	2.01
4	1.1	56.7	5.67	10.00	10.85	5.43	3.62	3.20	2.85	2.46
14	1.1	58	12	20.69	11.60	5.80	3.87	1.67	1.62	1.55
21	1.2	58.1	10.9	18.76	11.66	5.83	3.89	1.85	1.78	1.68
10	1.0	68	4.4	6.47	17.32	8.66	5.77	6.39	5.39	4.42
16	1.3	73.14	10.01	13.69	20.26	10.13	6.75	3.49	3.34	3.13
1	1.1	88	17	19.32	28.77	14.38	9.59	2.94	2.90	2.83
9	1.0	179*	35	19.55	80.84	40.42	26.95	4.03	4.02	3.99
Th [mg/kg]										
11	1.1	8.9	2.3	25.84	-6.76	-3.38	-2.25	2.10	1.85	1.58
13	1.1	11	2	18.18	-3.96	-1.98	-1.32	1.40	1.19	0.99

Table 4 continued…

Laboratory code	Technique code	Analyte concentration	Standard dev.	Relative std. dev., [%]	z-scores			u-scores		
					$k = 0.5$	$k = 1.0$	$k = 1.5$	$k = 0.5$	$k = 1.0$	$k = 1.5$
8	2.0	13.2	4	30.30	-1.04	-0.52	-0.35	0.19	0.18	0.17
12	1.2	14	3.6	25.71	0.03	0.01	0.01	0.01	0.01	0.00
15	1.1	14	3	21.43	0.03	0.01	0.01	0.01	0.01	0.01
7	1.1	14.7	3.7	25.17	0.96	0.48	0.32	0.19	0.18	0.17
20	1.1	16	2	12.50	2.69	1.34	0.90	0.95	0.81	0.67
					U [mg/kg]					
15	1.1	3	2	66.67	-3.91	-1.96	-1.31	0.51	0.49	0.48
8	2.0	4.6	3	65.22	2.22	1.11	0.74	0.19	0.19	0.19

Table 5. The combined *z*-scores for the participating laboratories.

Lab Code	Number of analytes	Rescaled sum of scores (RSZ)			Sum of squared scores (SSZ)			Critical value
		$k = 0.5$	$k = 1.0$	$k = 1.5$	$k = 0.5$	$k = 1.0$	$k = 1.5$	χ^2
1	18	-11.53	-5.77	-3.84	5827	1457	648	31.53
2	17	-13.07	-6.53	-4.36	983	246	109	30.19
3	19	-21.50	-10.75	-7.17	6391	1598	710	32.85
4	13	603.00	301.50	201.00	4896000	1224000	544000	24.74
5	14	3.25	1.63	1.09	1131	283	126	26.12
6	23	-0.20	-0.10	-0.07	6911	1728	768	38.06
7	14	4.81	2.41	1.60	1217	304	135	26.12
8	23	-8.16	-4.08	-2.72	3254	814	362	38.06
9	11	39.94	19.97	13.31	8620	2155	958	21.92
10	14	4.30	2.15	1.44	2191	548	244	26.12
11	15	-8.53	-4.26	-2.84	2002	501	223	27.49
12	23	-15.85	-7.93	-5.28	721	180	80	38.06
13	12	-0.98	-0.49	-0.33	67	17	7	23.34
14	15	-8.91	-4.45	-2.97	1716	429	191	27.49
15	27	21.50	10.75	7.17	41650	10410	4628	45.71
16	13	12.67	6.34	4.22	3075	769	342	24.74
17	3	26.78	13.39	8.93	1245	311	138	9.35
18	3	170.70	85.36	56.90	98280	24570	10920	9.35
19	3	-66.76	-33.38	-22.25	4675	1169	520	9.35
20	16	0.01	0.00	0.00	554	139	62	28.85
21	18	-4.30	-2.15	-1.43	4259	1065	473	31.53
22	11	-4.62	-2.31	-1.54	137	34	15	21.92

APPENDIX II

Figures 1-6

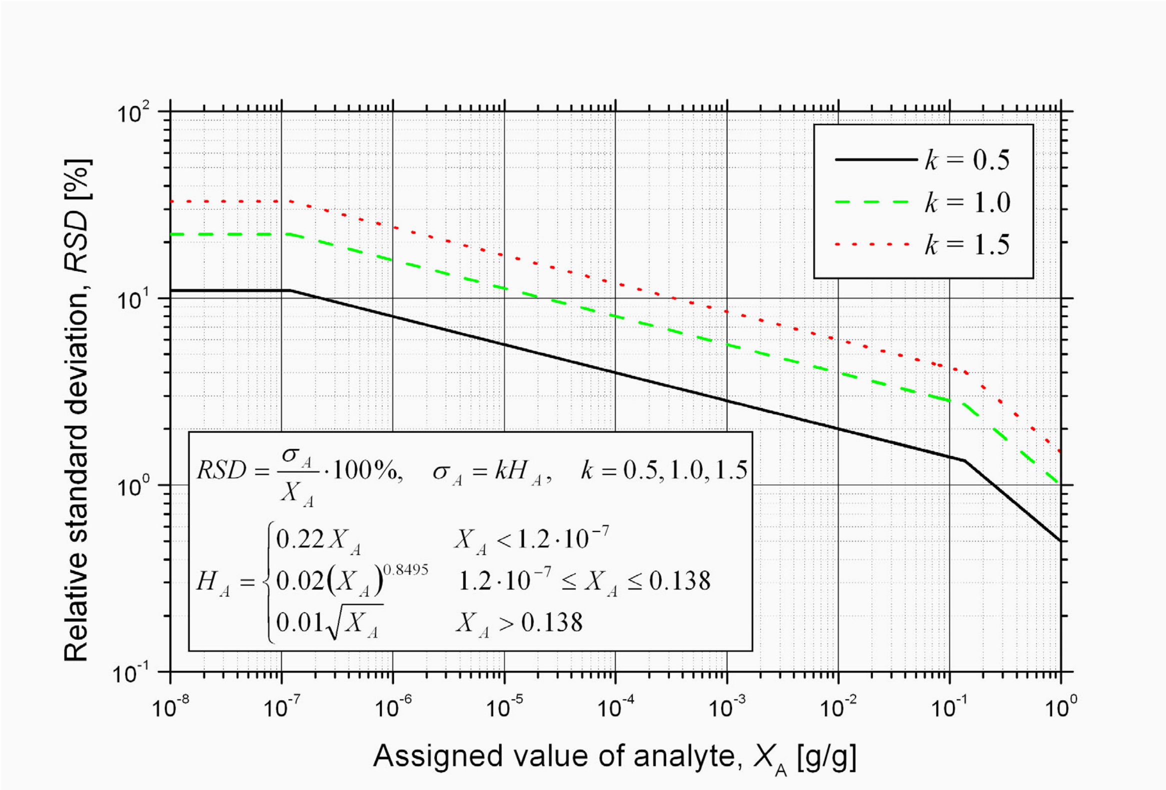


Fig. 1. Relative value of the target standard deviation, *RSD*, as a function of the assigned mass fraction of the analyte, X_A, calculated using a modified Horowitz function. The target value, σ_A, is related to H_A by a factor k and it is recognized as fit-for-purpose in three levels of uncertainty: $k = 0.5$ (solid black line), appropriate for high precision analysis; $k = 1.0$ (dashed green line), appropriate for well established routine analysis; $k = 1.5$ (dot red line), satisfactory for common analytical tasks.

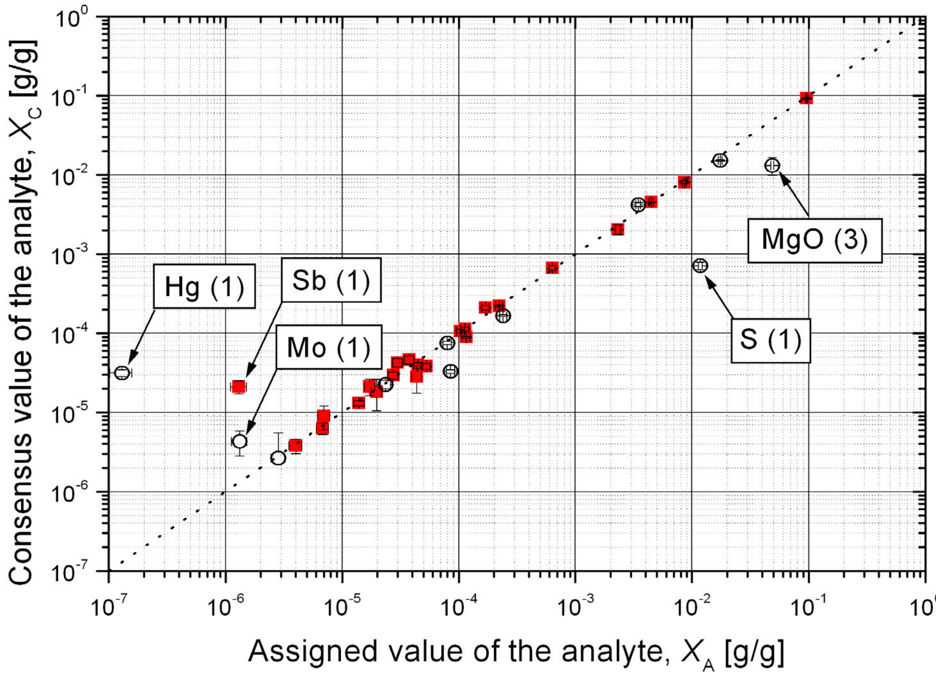


Fig. 2. The correlation between the assigned values of the analytes, X_A, and the consensus values, X_C, calculated from the reported results (solid red squares - the analytes for which the concentrations are recommended with relatively high or reasonable degree of confidence by IAEA-SL-1 certificate; hollow black circles – the analytes for which the concentrations are reported as information values in IAEA-SL-1 certificate). The analytes showing a weak correlation were labeled with the number of reported results given in brackets. The uncertainties of the assigned values shown on the graph were calculated according to Eqn. (2) with $k = 1$. The uncertainties of the consensus values were calculated using Eqn.(20), except for the results reported by single laboratory; in such a case the laboratory estimate of the uncertainty is shown.

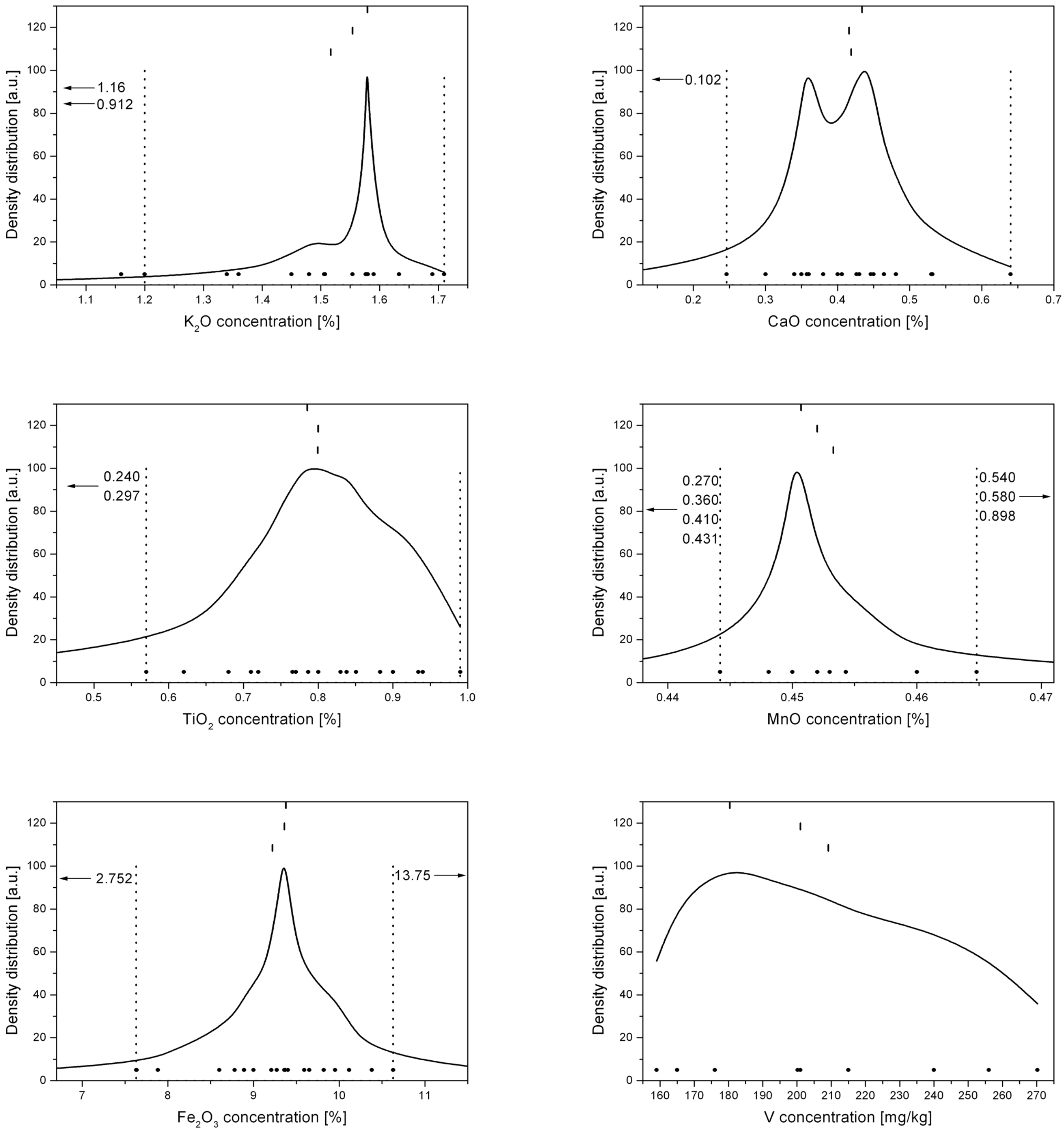


Fig. 3. The density distributions of the results for the analytes reported by at least 6 laboratories. The results are marked with filled circles. The dotted lines show the range of results accepted for calculating the consensus values, the outliers are reported and marked with arrows. Also marked, with markers positioned above the distribution curves, are the estimated parameters of the distribution: the mode, median and the mean value.

Fig. 3 continued…

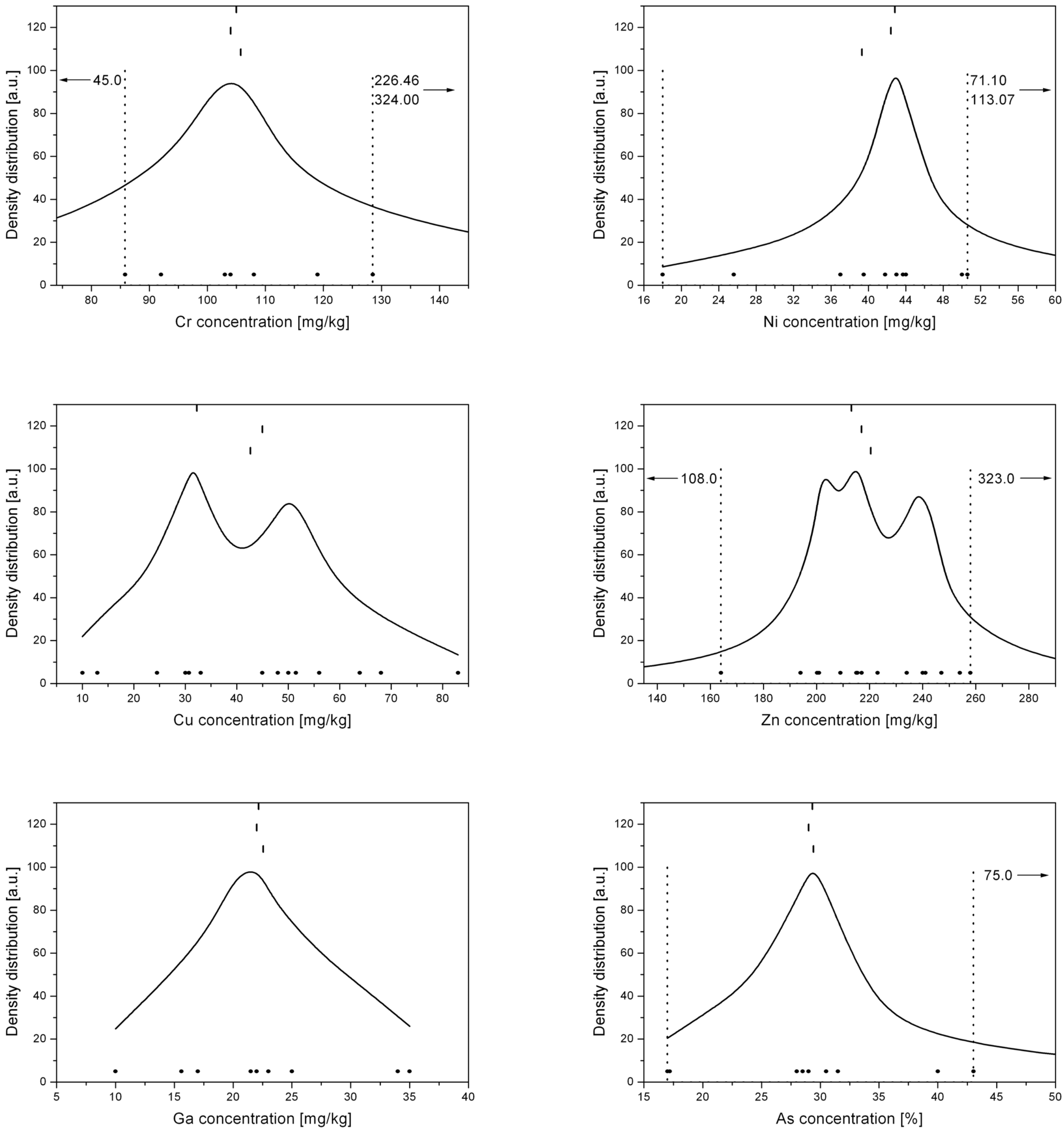


Fig. 3 continued…

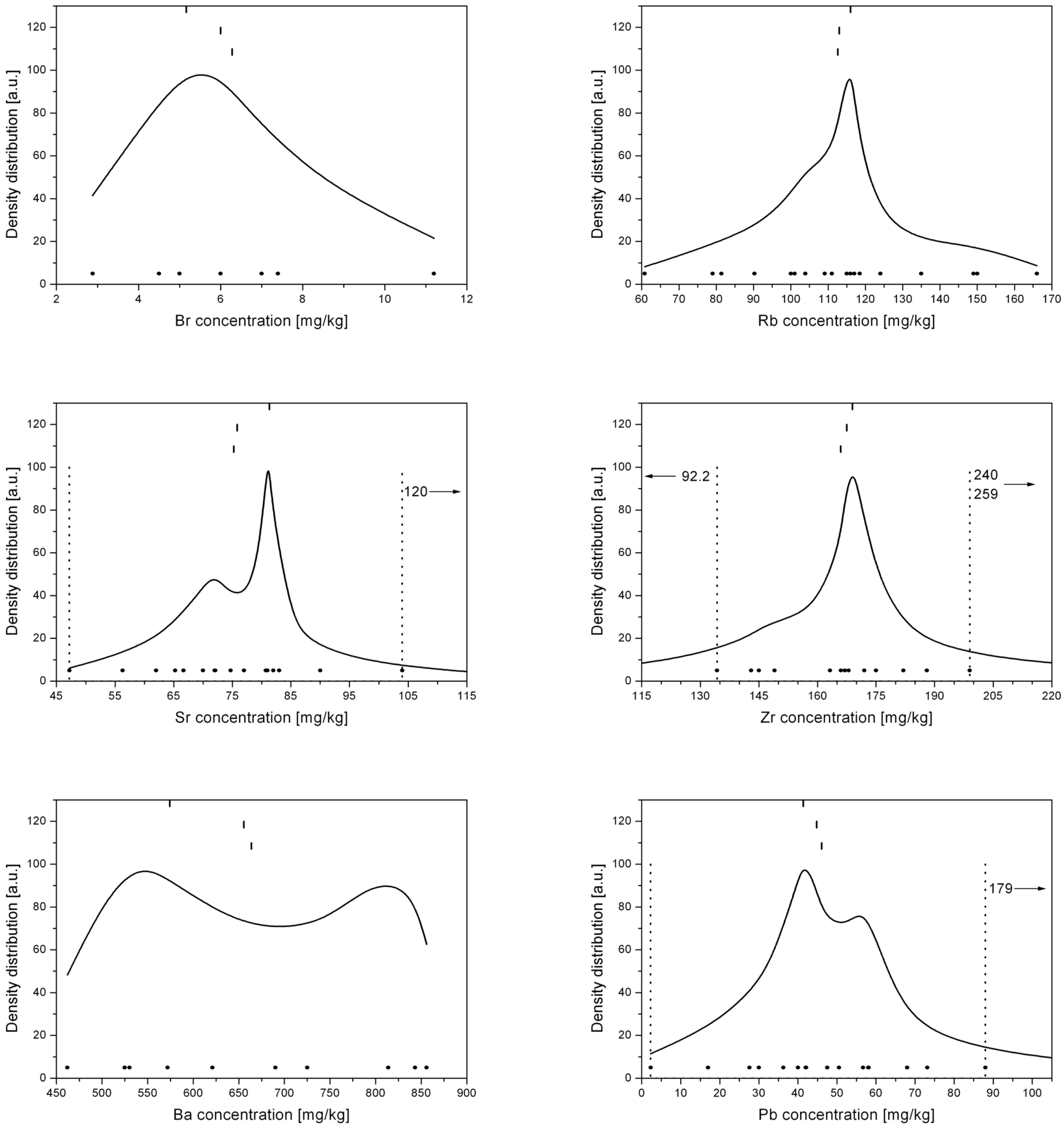
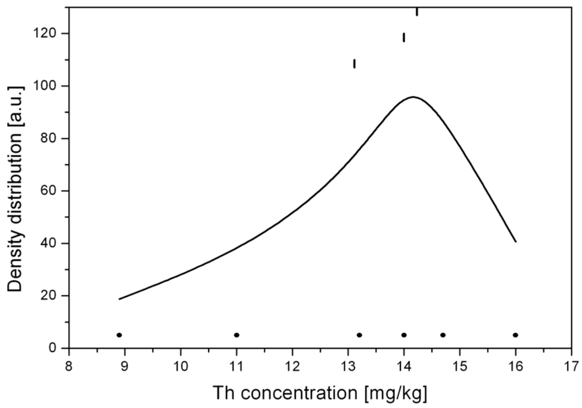


Fig. 3 continued…



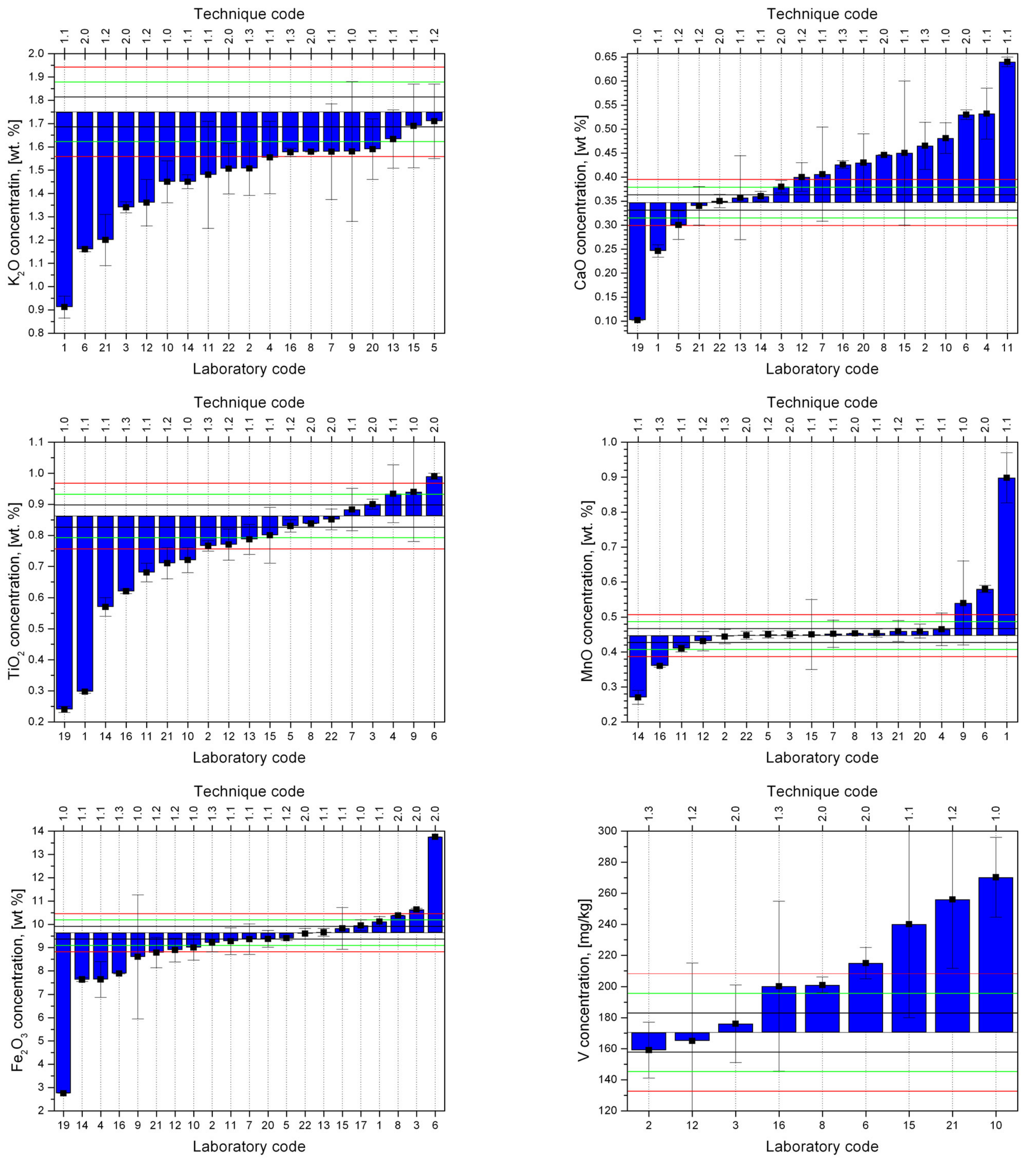


Fig. 4. The distribution of results for the analytes reported by at least 6 laboratories. The bar charts show the distance between the reported and the assigned value of the analyte. The reported values and their uncertainties, as provided by the analyst, are marked with the filled squares accompanied by uncertainty bars. The horizontal lines show the acceptable levels of z-score, $|z| < 2$, for three different fit-for-purpose ranges defined by factor k in Eqn. (2): $k = 0.5$ (solid black lines), $k = 1.0$ (solid green lines), and $k = 1.5$ (solid red lines).

Fig. 4 continued…

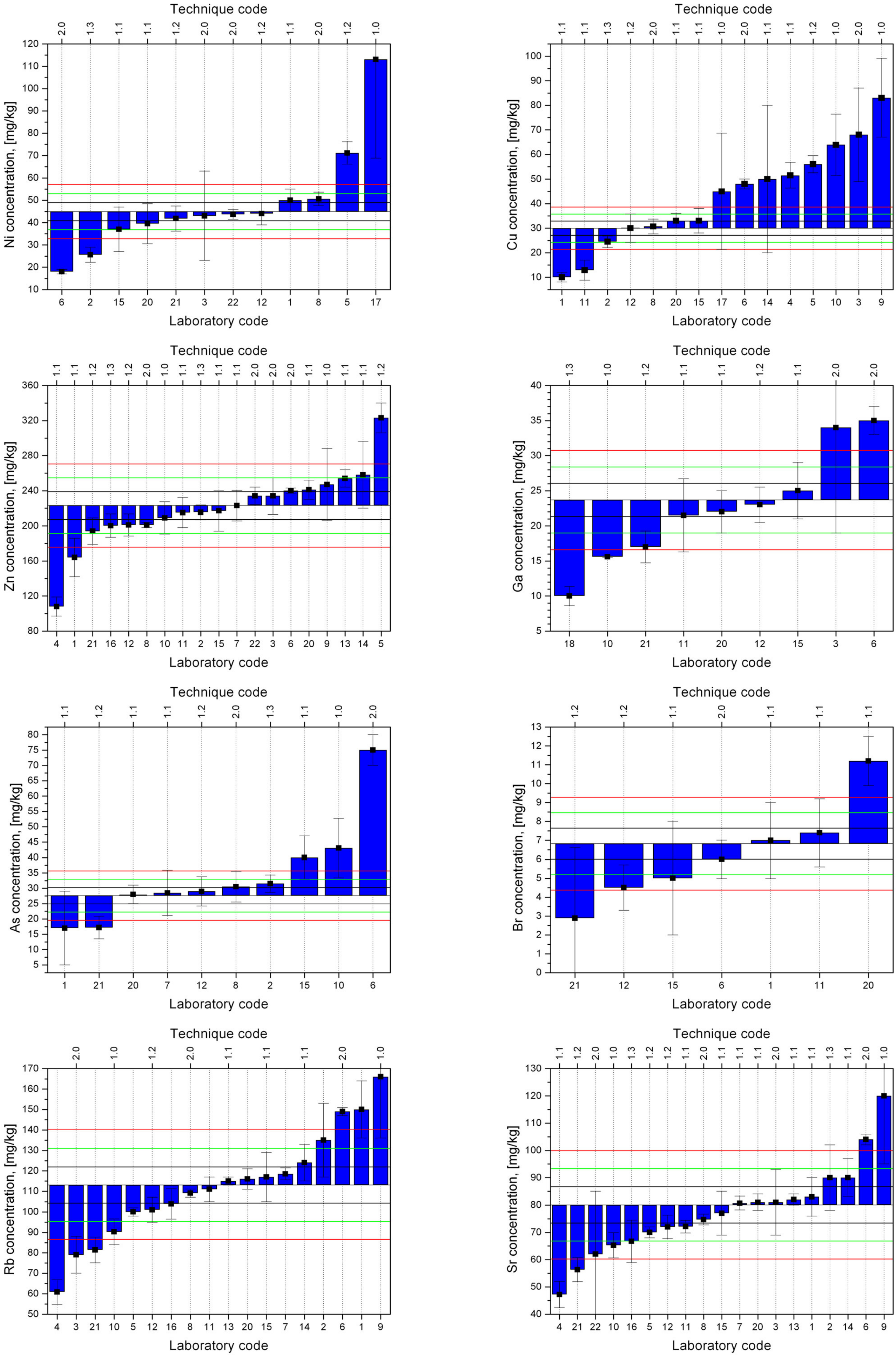
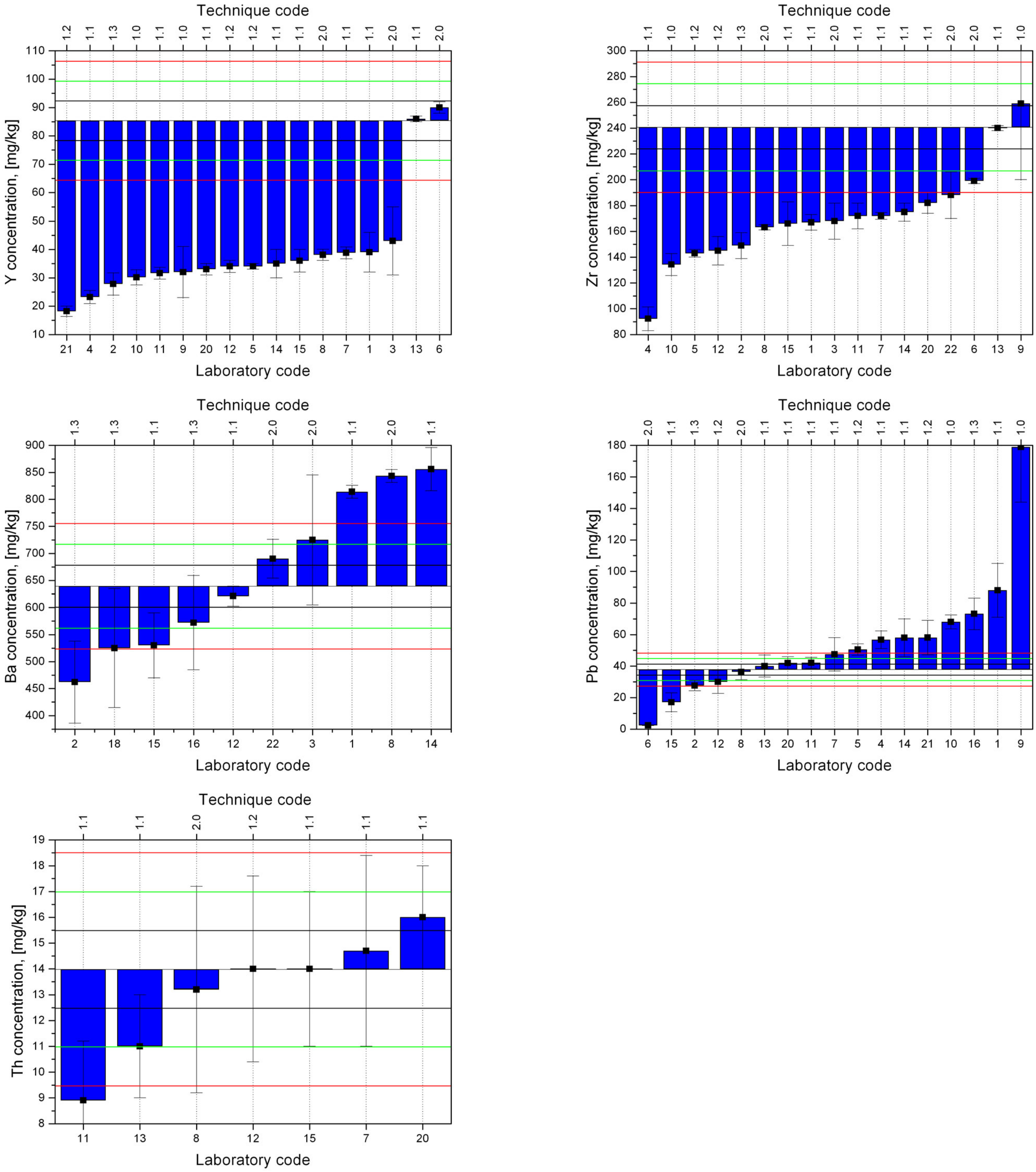


Fig. 4 continued…



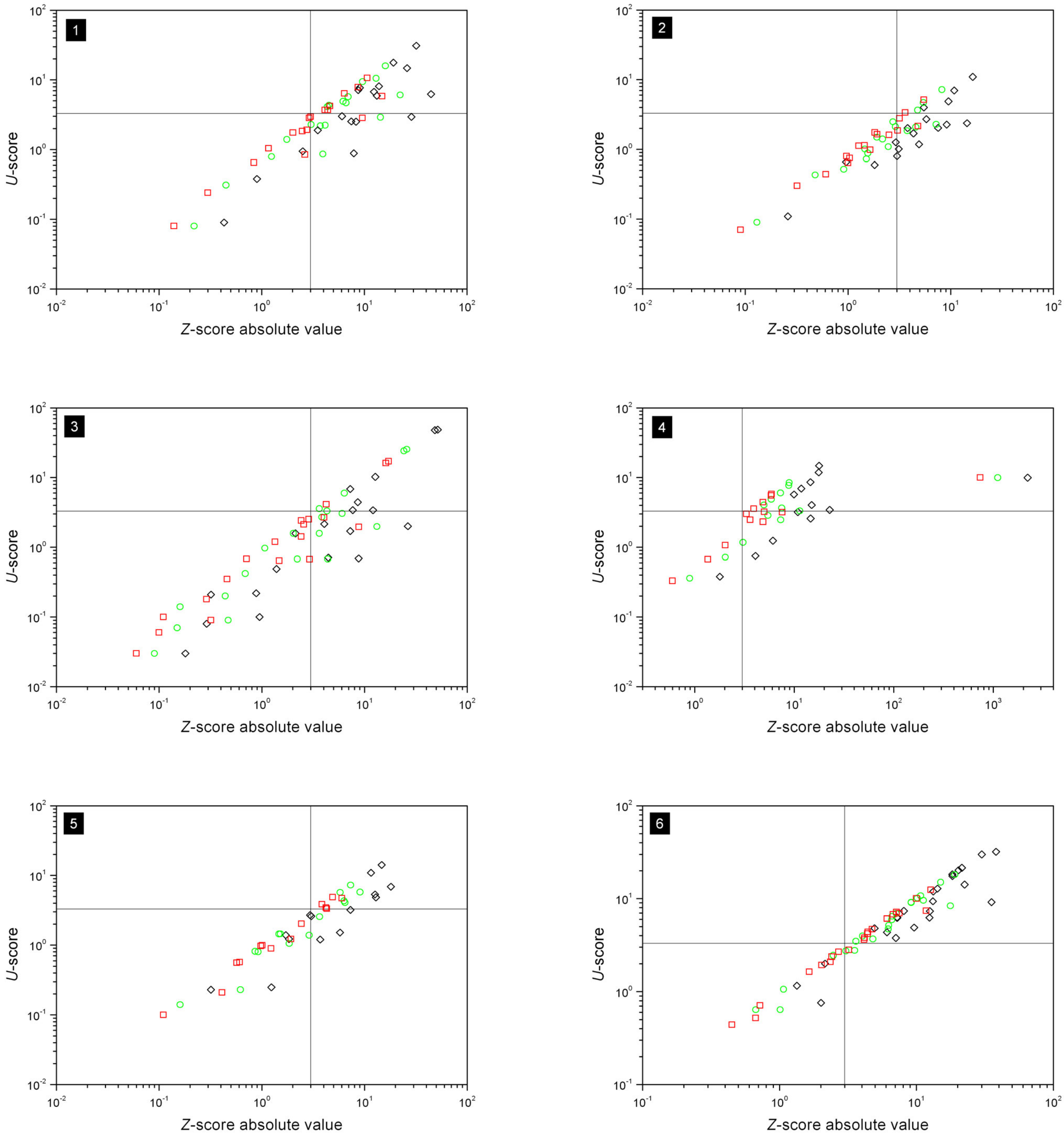


Fig. 5. Combined plots of z-scores and u-scores for participating laboratories. The laboratory code is shown in left upper corner of each plot. The hollow symbols denote the values calculated for specific fit-for-purpose levels as defined in Eqn. (2); $k = 0.5$ (black diamond symbols), $k = 1.0$ (green circle symbols), and $k = 1.5$ (red square symbols). The solid lines mark the decision level for z-score, $|z| = 3$, and u-score, $u = 3.29$.

Fig. 5 continued…

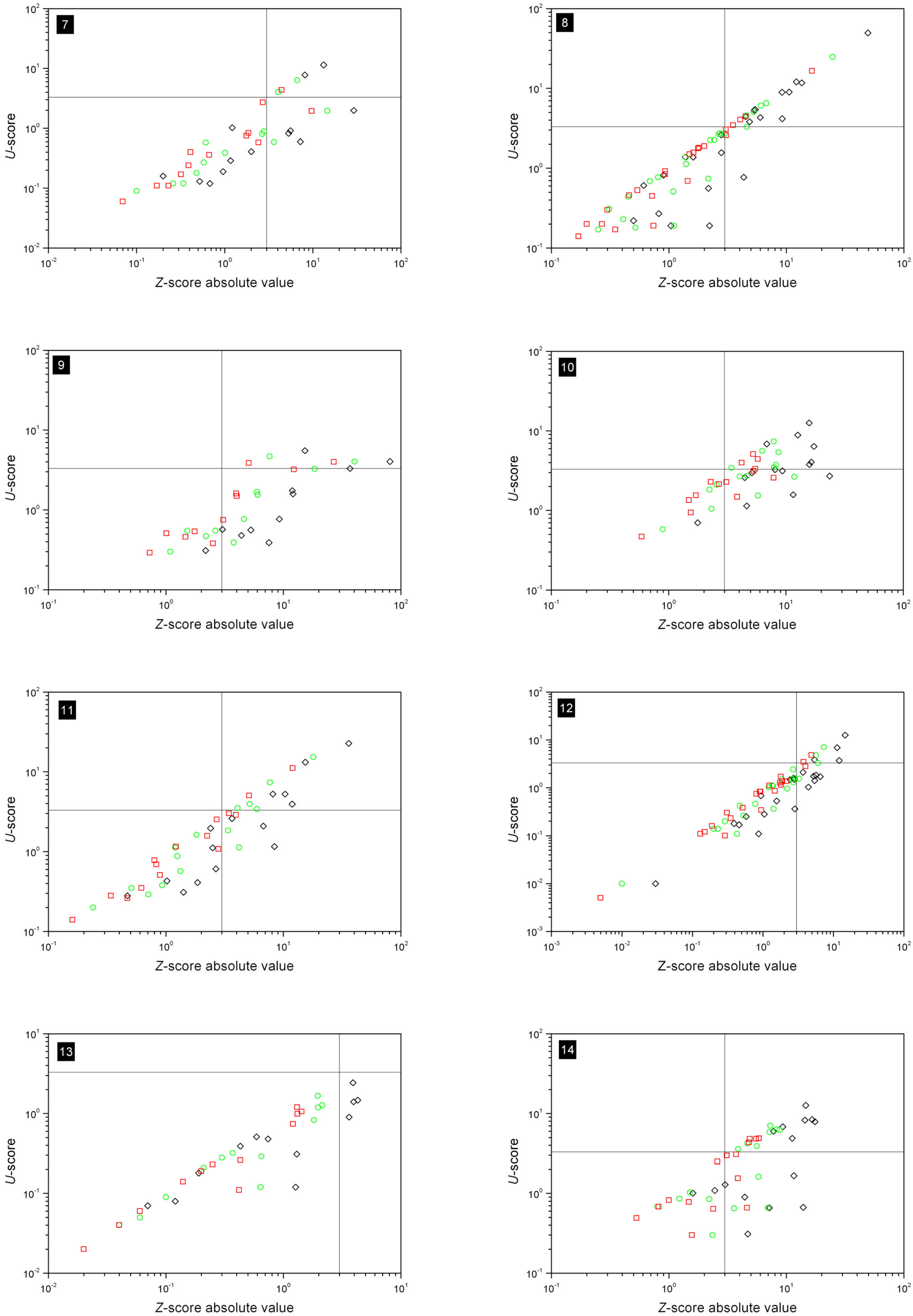
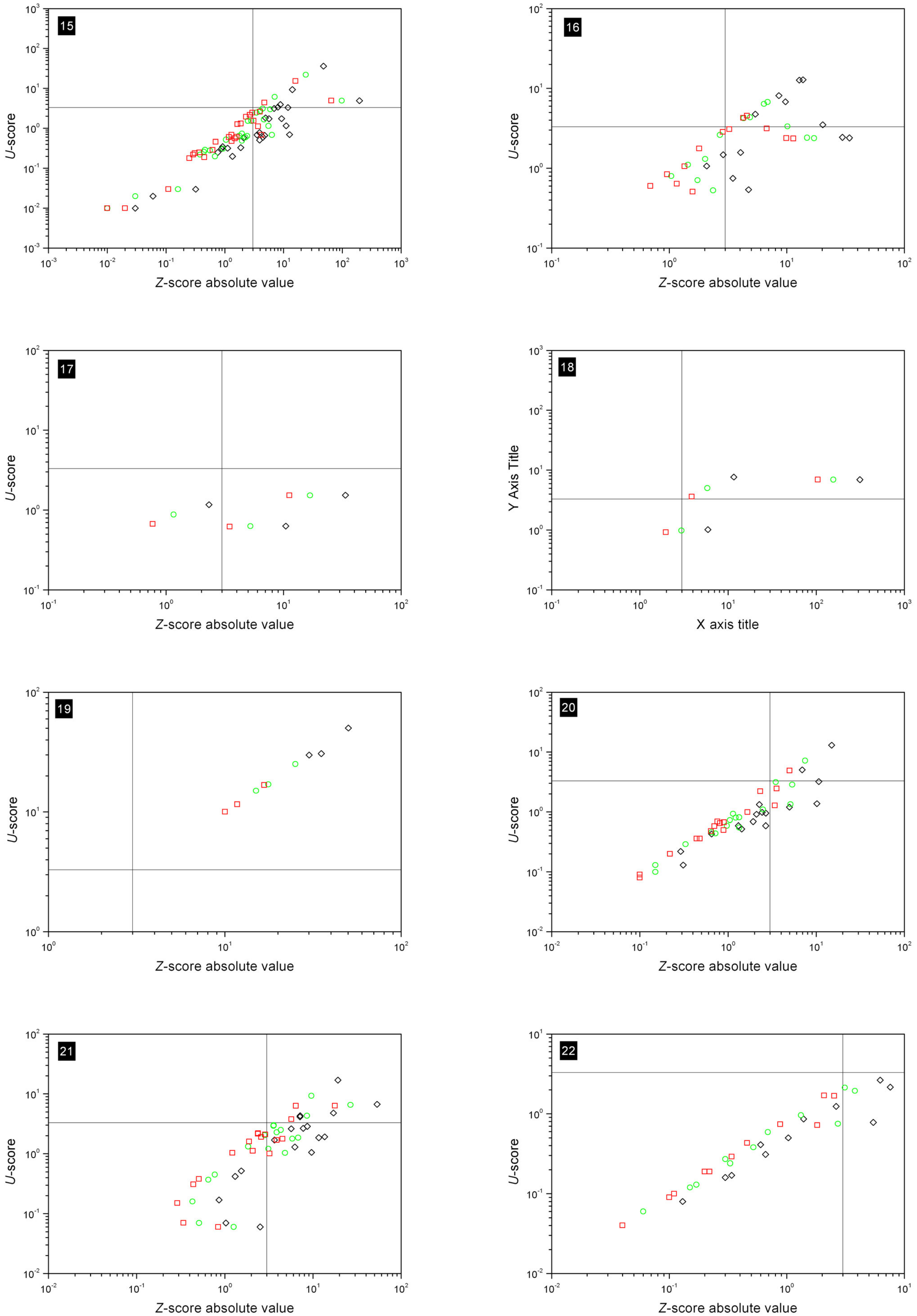


Fig. 5 continued…



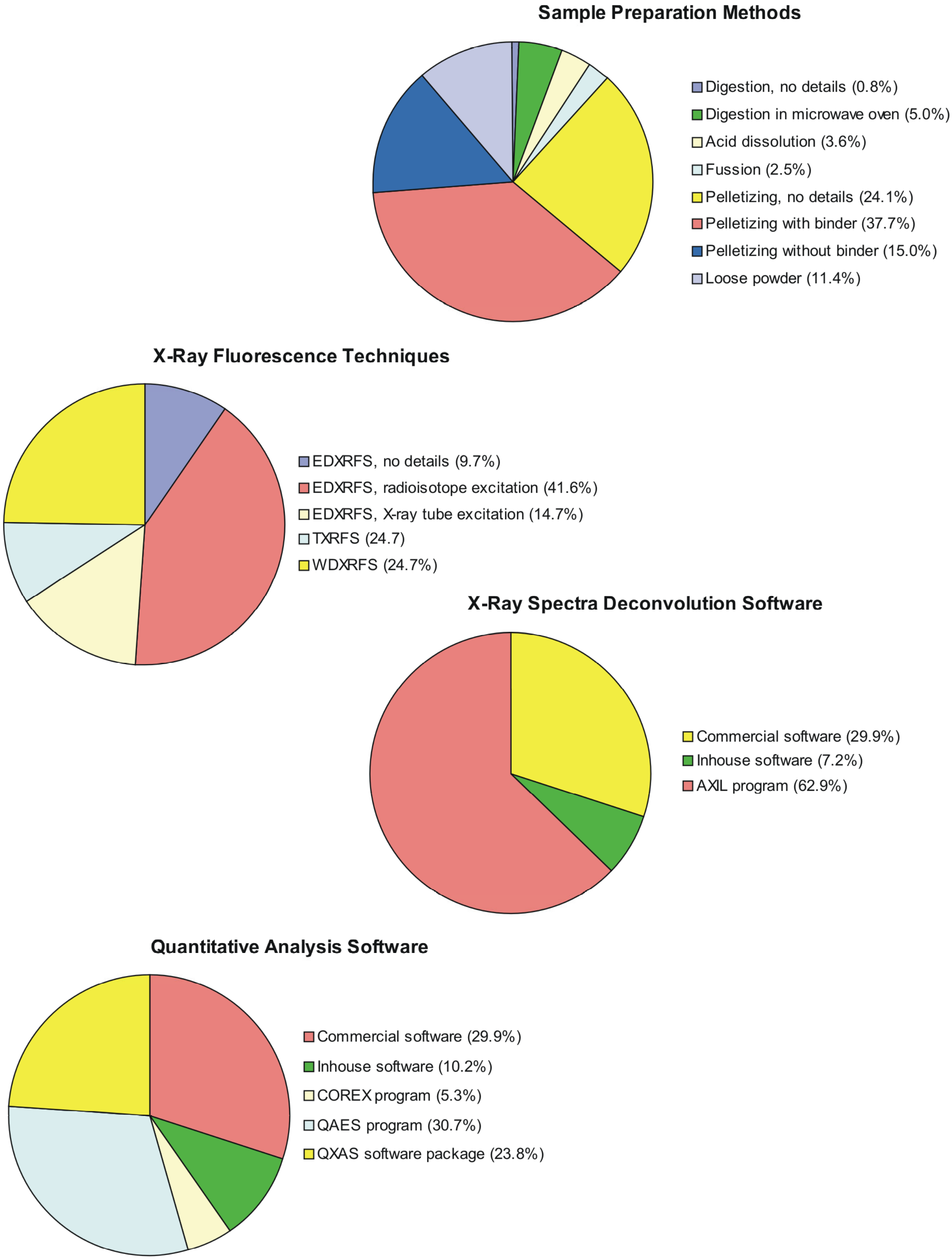


Fig. 6. Percentage utilization of the techniques, methods of sample preparation, X-ray spectra deconvolution and quantitative analysis software as reported by the participants of the proficiency test exercise. The per cent values refer to the total number (361) of the submitted results.